MODELING & OPTIMISATION OF COARSE MULTI-VESICULATED PARTICLES

by

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Abstract

Multi-vesiculated particles (MVP) are synthetic insoluble polymeric particles containing a multitude of vesicles (micro-voids). The particles are generally produced and used as a suspension in an aqueous fluid and are therefore readily incorporated in latex paints as opacifiers. The coarse or suede MVP have a large volume-mean diameter (VMD) generally in the range of 35-60µm, the large VMD makes them suitable for textured effect paints.

The general principle behind the MVP technology is as the particles dry, the vesicles drain of liquid and fill with air. The large refractive index difference between the polymer shell and air result in the scattering of incident light which give the MVP their white opaque appearance making them suitable as an opacifier for the partial replacement of TiO_2 in coating systems.

Whilst the coarse MVP have been successfully commercialized, insufficient understanding of the influence of the MVP system parameters on the final MVP product characteristics coupled with the MVP's sensitivity towards the unsaturated polyester resin (UPR) resulted in a product with significant quality variation. On the other hand these uncertainties provided the opportunity to model and optimise the MVP system through developing a better understanding of the influence of the MVP system parameters on the MVP product characteristics, developing a model to mathematically describe these relationships and to optimise the MVP system to achieve the product specifications whilst simultaneously minimising the variation observed in the product characteristics.

The primary MVP characteristics for this study were the particle size distribution (quantified by the volume-mean diameter (VMD)) and the reactor buildup.[1]

The approach taken was to analyse the system determining all possible system factors that may affect it, and then to reduce the total number of system factors by selecting those which have a significant influence on the characteristics of interest. A model was then developed to mathematically describe the relationship between these significant factors and the characteristics of interest. This was done utilising a set of statistical methods known as design of experiments (DoE).

A screening DoE was conducted on the identified system factors reducing them to a subset of factors which had a significant effect on the VMD & buildup. The UPR was characterised by its acid value and viscosity and in combination with the identified significant factors a response surface model (RSM) was developed for the chosen design space, mathematically describing their relationship with the MVP characteristics. Utilising a DoE method known as robust parameter design (specifically propagation of error) an optimised MVP system was numerically determined which brought the MVP product within specification and simultaneously reduced the MVP's sensitivity to the UPR.

The validation of the response surface model indicated that the average error in the VMD prediction was 2.16µm (5.16%) which compared well to the 1.96µm standard deviation of replication batches. The high Pred-R^2 value of 0.839 and the low validation error indicates that the model is well suited for predicting the VMD characteristic of the MVP system. The application of propagation of error to the model during optimisation resulted in a MVP process and formulation which brought the VMD response from the standard's average of 44.56µm to the optimised system's average of 47.84µm which was significantly closer to the desired optimal of 47.5µm. The most notable value added to the

[1] Buildup is a visually estimated measure of the degree to which gel-like polymer lattice forms along the edge of the reactor. It is an undesirable characteristic of the process.

system by the propagation of error technique was the reduction in the variation around the mean of the VMD, due to the UPR, by over 30%[1] from the standard to optimised MVP system.

In addition to the statistical model, dimensional analysis, (specifically Buckingham-Π method) was applied to the MVP system to develop a semi-empirical dimensionless model for the VMD. The model parameters were regressed from the experimental data obtained from the DoE and the model was compared to several models sited in literature. The dimensionless model was not ideal for predicting the VMD as indicated by the R^2 value of 0.59 and the high average error of 21.25%. However it described the VMD better than any of the models cited in literature, many of which had negative R^2 values and were therefore not suitable for modelling the MVP system.

[1] based upon the coefficient of variation.

Opsomming

Sintetiese polimeer partikels wat veeltallige lugblasies huisves en omhul, staan beter bekend as MVP (verkort vanaf die Engelse benaming, "multi-vesiculated particles"). Tipies word hierdie partikels berei en gestabiliseer in 'n waterige suspensie wat dit mengbaar maak met konvensionele emulsie sisteme en dit dus in staat stel om te funksioneer as 'n dekmiddel in verf. Deur die volume gemiddelde deursnee (VGD) te manipuleer tot tussen 35 en 60µm, word die growwe partikels geskik vir gebruik in tekstuur verwe, soos byvoorbeeld afwerkings met 'n handskoenleer (suède) tipe tekstuur.

Die dekvermoë van MVP ontstaan soos die partikels droog en die water in die polimeer partikel vervang word met lug. As gevolg van die groot verskil in brekingsindeks tussen die polimeer huls en die lugblasies, word lig verstrooi in alle rigtings wat daartoe lei dat die partikels wit vertoon. Dus kan die produk gebruik word om anorganiese pigmente soos TiO_2 gedeeltelik te vervang in verf.

Alhoewel growwe MVP al suksesvol gekommersialiseer is, bestaan daar nog net 'n beperkte kennis oor die invloed van sisteem veranderlikes op die karakteristieke eienskappe van die finale produk. Dit volg onder andere uit waarnemings dat die kwaliteit van die growwe MVP baie maklik beïnvloed word deur onbekende variasies in die reaktiewe poliëster hars wat gebruik word om die partikels te maak. Dit het egter die geleentheid geskep om die veranderlikes deeglik te modeleer en te optimiseer om sodoende 'n beter begrip te kry van hoe eienskappe geaffekteer word. 'n Wetenskaplike model is opgestel om verwantskappe te illustreer en om die sisteem te optimiseer sodat daar aan produk spesifikasies voldoen word, terwyl produk variasies minimaal bly.

Die oorheersende doel in hierdie studie was om te fokus op partikelgrootte en verspreiding (bepaal met behulp van die VGD) as primêre karakteristieke eienskap, asook die graad van aanpaksel op die reaktorwand gedurende produksie.

Vanuit eerste beginsel is alle moontlike veranderlikes geanaliseer, waarna die hoeveelheid verminder is na slegs dié wat die karakteristieke eienskap die meeste beïnvloed. Deur gebruik te maak van eksperimentele ontwerp is die wetenskaplike model ontwikkel wat die effek van hierdie eienskappe statisties omsluit.

'n Afskerms eksperimentele ontwerp is uitgevoer om onbeduidende veranderlikes te elimineer van dié wat meer betekenisvol is. Die hars is gekaraktiseer met 'n getal wat gebruik word om die aantal suur groepe per molekuul aan te dui, asook die hars se viskositeit. Hierdie twee eienskappe, tesame met ander belangrike eienskappe is gebruik om 'n karakteristieke oppervlakte model te ontwikkel wat hul invloed op die VGD van die partikels en reaktor aanpakking beskryf. Deur gebruik te maak van 'n robuuste ontwerp, beter beskryf as 'n fout verspreidingsmodel, is die MVP sisteem numeries geoptimiseer. Dit het tot gevolg dat die MVP binne spesifikasie bly en die VGD se sensitiwiteit vir variasie in die hars verminder het.

Geldigheidstoetse op die oppervlakte model het aangetoon dat die gemiddelde fout in VGD 2.16µm (5.16%) was. Dit is stem goed ooreen met die 1.96µm standaard afwyking tussen herhaalde lopies. Hoë Pred-R^2 waardes (0.839) en lae geldigheidsfout waardes het getoon dat die voorgestelde model die VGD eienskappe uiters goed beskryf. Toepassing van die fout verspreidingsmodel gedurende optimisering het tot gevolg dat die VGD vanaf die standaard gemiddelde van 44.56µm verskuif het na die geoptimiseerde gemiddelde van 47.84µm. Dit is aansienlik nader aan die verlangde optimum waarde van 47.5µm. Die grootste waarde wat toegevoeg is na afloop van hierdie studie, is dat die

afwyking rondom die gemiddelde VGD, toegeskryf aan die eienskappe van die hars, verminder het met oor die 30%[1] (vanaf die standaard tot die optimiseerde sisteem).

Verdere dimensionele analise van die sisteem deur spesifiek gebruik te maak van die Buckingham-Π metode het gelei tot die ontwikkeling van 'n semi-empiriese dimensielose VGD model. Regressie op eksperimentele data verkry uit die eksperimentele ontwerp is vergelyk met verskeie modelle beskryf in ander literatuur bronne. Hierdie dimensionele model was nie ideaal om die VGD te beskryf nie, aangesien die R^2 waarde 0.59 was en die gemiddelde fout van 21.25% relatief hoog was. Nietemin, hierdie model beskryf die VGD beter as enige ander model voorgestel in die literatuur. In talle gevalle is negatiewe R^2 waardes verkry, wat hierdie literatuur modelle geheel en al ongeskik maak vir toepassing in die MVP sisteem.

[1] Gebaseer op die afwykingskoëffisiënt.

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Dedicated to my son, Trystan

Daddy will have more time to play now

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List of Abbreviations

%CV	Coefficient of Variance
%NVC	Non-Volatile Content
%TSC	Total Solids Content
2FF	Two-Level Fractional Factorials
BBD	Box-Behnken Design
CHP	Cumene Hydroperoxide
CP	Cone and Plate
CR	Contrast Ratio
d_{32}	Sauter-Mean Diameter
d_{43}	De Brouckere-Mean Diameter
DAE	Dimensional Analysis Empirical
DETA	Diethylene Triamine
DM	Dimensionless Model
DX7®	Design Expert® 7
FF	Fractional Factorial
HASE	Hydrophobically Modified Alkali Swellable Emulsion
HEC	Hydroxy-Ethyl Cellulose
IFT	Interfacial Tension
LMA	Lauryl Methacrylate
MVP	Multi-Vesiculated Particles
OFAT	One-Factor-At-a-Time
PBE	Population Balance Equations
PoE	Propagation of Error
PSD	Particle Size Distribution
PVOH	Hydrolysed Poly(Vinyl Acetate)
QA	Quality Assurance

RPD	Robust Parameter Design
RSM	Response Surface Method
	Response Surface Methodology
SDev	Standard Deviation
SG	Specific Gravity
SMD	Sauter-Mean Diameter
TiO_2	Titanium Dioxide
UPR	Unsaturated Polyester Resin
VMD	Volume-Mean Diameter
VP	Vesiculated Particles

Nomenclature specific to each section is listed at the end of each chapter.

1. Introduction

1.1 Background

Paint is a complex fluid consisting of a mixture of a liquid vehicle (binder & thinner), pigments and additives. The global paint & coatings industry is a multi-billion dollar industry which in 2009 was valued at $91.7billion, with the architectural & decorative coatings segment valued at $38.1billion (41.5%); having an expected growth of 15.4% by 2014 (Datamonitor, 2010). The raw materials, energy & labour contributes approximately 60% to the final value of each litre of paint (Challener, 2009) and therefore research into reducing the raw material costs can add significant value to this industry.

Paint Composition & Function:

The Binder forms the film and binds the pigments. It gives the finished coating its adhesion, durability, and protective properties (“SAPMA…”, 2000). The thinner can either be a solvent or a diluent which is primarily used to obtain the required rheological properties of the paint which are critical to the formation of a coating film. Additives are used to overcome defects in the paint system or to improve the overall performance (Scholz, 1993). The most common classes of additives are wetting and dispersion additives, surface additives, defoamers, preservatives, rheology modifiers, ultraviolet stabilizers and driers (Scholz, 1993). The pigments contribute to the durability and to produce the required optical properties of the coating in terms of gloss, opacity and colour. Subcategories of pigments, known as extenders, have poor colour and opacifying properties but are used to reduce the cost of the formulation and modify the durability and protective properties of the paint.

One of the main functions of an architectural top coat is to decorate the surface of the substrate. This can be done by obliterating the substrate via the paints opacity, providing colour and/or adding effects whether gloss level, metallic, pearlescent, or textured. These effects are significantly determined by the type and quantity of pigment used. The most commonly used pigment is Titanium Dioxide (TiO_2) due to its high refractive index and ability to reflect almost the entire visual light spectrum in its original composition (Walton, 1993). The opacity which the TiO_2 imbues on to the coating is due to the high refractive index difference between the pigment and the binder. The cost and demand for TiO_2 is steadily rising which is forcing the paint industry to look for alternative methods and/or pigments to replace the dwindling and expensive TiO_2 pigments. One such alternative is the Vesiculated Particles (beads) Technology.

1.2 Vesiculated Particles (VP)

Vesiculated particles are synthetic insoluble polymeric particles containing vesicles (micro-voids). The particles are generally manufactured and used as a suspension in an aqueous fluid. Two types of VP are available, the single void, mono-vesiculated particles, for example, Ropaque® Opaque Polymer, and the multi-void, Multi-Vesiculated Particles (MVP) such as Spindrift® (Stewart & Ritchie, 1993).

The general principle behind the VP technology is as the particles dry, the vesicles drain of liquid and fill with air. The large refractive index difference between the polymer shell and the air result in the scattering of incident light and provides the VP with its white opaque appearance. VP are produced as a dispersion in an aqueous continuous phase and therefore can be readily incorporated in latex paints as opacifiers. The technology of incorporating air in a paint film has been used for decades in above critical-PVC (pigment volume concentration) paints (Stewart & Ritchie, 1993). The novel idea was to incorporate air in stable polymeric particles for use in Latex paint systems for all PVC ranges.

A type of MVP was developed by a local member of the NOVA Paint Club, from technology originally developed within the group. The advantage of this MVP product is the ability to vary the particle size distribution from a Sauter-Mean Diameter (SMD) of 0.5micron used in gloss paints to a SMD of between 4 to 10 microns for matt paints and up to 40 microns for textured effect paint. The matt and textured products have been successfully developed and commercialized within South Africa.

The MVP process is however, currently suboptimal and susceptible to significant variation due to the batch-to-batch variation of the unsaturated polyester resin (UPR) used in the process (Terblanche 2002). Therefore there is significant room to optimise the process and reduce the variation experienced with batch-to-batch variation of this raw material.

1.3 Problem Statement

Freeworld Coatings Plascon in collaboration with the Department of Process Engineering at the University of Stellenbosch has successfully commercialised the production of multi-vesiculated particles (MVP) for a single emulsification batch process (Terblanche, 2002; Gous, 2003). However many unknowns about the process still remain.

Coarse particle sized (Suede) MVP have been commercialized for effect paints. However, the process has not yet been optimised and there is still insufficient understanding of the process for accurate quality control. The knowledge of the contribution of each raw material and their interacting effects to the final MVP product needs to be better understood to optimise the process and improve the control over the MVP product. The current wait-and-see approach for quality assurance (QA) results in the high likelihood that a 10ton batch may not meet specification. If this occurs the batch will be rejected which becomes a time consuming, and costly process with negative environmental effects.

Of further concern is even if the UPR was manufactured to specification there is still considerable batch-to-batch variation influence on the MVP. This creates the problem that the UPR still needs to be tested in a bench-scale batch of MVP before accepting the UPR for use commercially.

1.4 Modelling & Optimization Requirements

In the 1980's Dr. Genichi Taguchi redefined the approach to modelling and optimising quality. Taguchi argued that quality should be seen as reducing the loss to society and he promoted the philosophy that quality should not only meet a specific target but have minimum deviation from the target (Rekab & Shaik, 2005).

The MVP developed by Terblanche (2002) are not yet robust to variations in the UPR raw material and therefore according to Taguchi's philosophy significant quality loss is incurred due to this variation. Thus, the process and formulation needs to be optimised to be as robust to the variation of the UPR as possible.

As with many novel, complex, multi-component systems there is often a significant lack of appropriate knowledge of the fundamental aspects of the mechanisms, kinetics, and thermodynamics needed for a fundamentally based model of the process. Therefore, empirical data and modelling is essential for developing and optimising these complex processes. This is true of the effect of the UPR on the MVP characteristic properties especially the particle size distribution and contrast ratio. There is currently no quantitative, fundamental or empirical, understanding of the mechanism or influence of the UPR on the MVP.

Thus an empirical understanding of the UPR influence on the MVP would go a long way to solving the optimisation problem of the MVP and reduce the MVP sensitivity, to the variation between the UPR batches.

1.5 Objectives

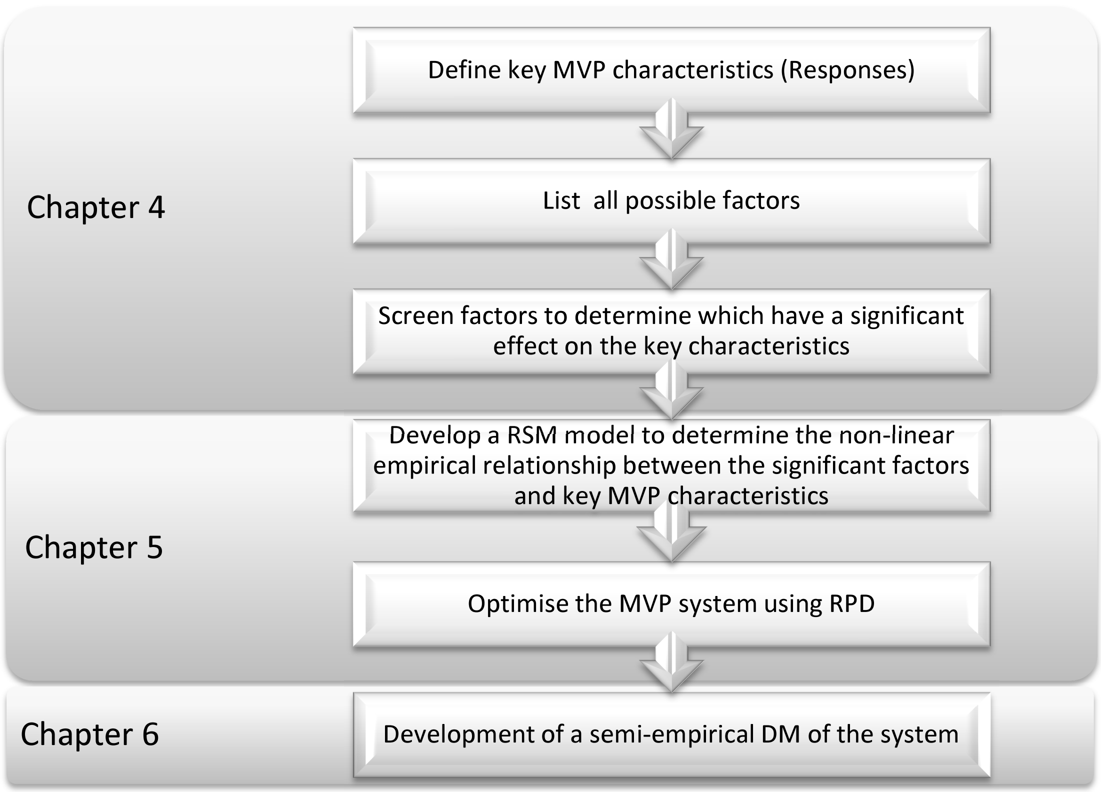
The proposed objectives of this project are to (1) create a better understanding of the contribution of each system variable to the MVP product, (2) to develop a model which could be used to optimise the process and (3) to indicate the requirements for control over the process which would lead to a reproducible product robust against the variations experienced due to the UPR.

The proposed work involved the following stages:

1. Define the key characteristics of the Suede MVP and then use a screening design of experiments (DoE) to determine which processing variables and raw materials affect the key properties. (**Chapter 4**).
    - <u>Outcome:</u> Better understanding of the raw materials and process and how each variable affects the final product. A better understanding of the variable tolerances of the process will indicate where increased control over the system will be required.
2. Once a better understanding of the system parameters is obtained the current formulation & process will then be modelled using response surface methodology (RSM) DoE. The RSM model will be validated experimentally (**Chapter 5**).
    - <u>Outcome:</u> A non-linear RSM model for predicting properties of the MVP product based upon the MVP system input variables' level.
3. Robust parameter design (RPD) will be applied to the RSM model to optimise the MVP product by increasing the robustness of the system as a whole; with, particular focus on minimising the variation caused by the UPR (**Chapter 5**).
    - <u>Outcome:</u> An optimised system which should increase the consistency of the product.

4. The above proposed model is based only upon a statistical analysis developed using a method called Design of Experiments. This approach has significant practical value but does not directly represent the physical phenomena of the MVP system. Therefore in order to obtain a better representation of the physical system a dimensional analysis will be conducted on the experimental data to develop a model based upon relevant engineering dimensionless groups. This representation of the physical system can be used as a basis for future work on a scale-up model for the MVP system.
   - Outcome: A semi-empirical dimensionless model (DM) based upon the Buckingham-Π method. (**Chapter 6**).

Figure 1. 1: Thesis Objectives & Layout



2 Literature Review

2.1 Introduction

Micro-air-void technology has been used for decades in above critical pigment volume concentration[1] (PVC) paints as a means for increasing opacity (Stewart, 1993). The difference in the refractive index between the polymer and the encased air-void, results in significant light scattering which increases the opacity of the coating. Polymeric particles which contain micro-voids can be used to achieve the advantages of adding micro-air-voids to a film without the disadvantages associated with formulating a film above the critical-PVC (Ritchie, 1993).

Various Vesiculated Particles technologies have been developed and patented. Three VP technologies that were commercialized for the coatings industry will be discussed; Firstly, the mono-vesicle Ropaque® Opaque Polymer developed by Rohm & Haas® and secondly the multi-vesiculated Spindrift® Developed by Dulux. Finally, as the focus of this thesis, the Multi-Vesiculated Polymer Particles (Hereinafter referred to as MVP) developed by Freeworld Coatings (Formerly Barloworld Coatings) will be reviewed.

2.2 Vesiculated Particles

2.2.1 Patented Technology

2.2.1.1 Vesiculated Cross-Linked Polyester Resin Granules

One of the earliest patents filed for vesiculated granules was granted to Gillian & Kershaw (1969). It describes the process of preparing vesiculated polymer granules comprising of a plurality of vesicles. The patent describes how to achieve granules of a specific pre-determined size from 0.1 to 500microns prepared from the cross-linking of an unsaturated polyester resin with an unsaturated monomer. The granules are suggested for use as an opacifier in surface coatings. Gillian & Kershaw (1969) described a typical example of preparing the vesiculated granules as follows:

> An unsaturated polyester resin (UPR) was prepared from a 3:1:4 molar ratio of fumeric acid, phthalic anhydride and propylene glycol, respectively. The UPR was prepared as a 70% by mass solution in xylene with an acid value of 44mg KOH per gram UPR and a Gardner-Holdt viscosity of T.
>
> The suitability of the UPR was confirmed by creating a stable water-in-oil emulsion of less than 5µm diameter droplets; by adding 5% by mass ammonia solution to a 60% mixture of UPR in xylene. The quantity of ammonia determined as the molar equivalent amount calculated on the carboxyl groups of the UPR.
>
> A mixture of 18.0 parts of UPR, 0.5 parts of benzoyl peroxide and 12.0 parts of styrene was dispersed under high speed in an aqueous solution of 4.06 parts hydroxyl ethyl cellulose, 7.28 parts of poly(vinyl acetate/alcohol) which is 80% hydrolysed, in 719.0 parts water with 2.0 parts diethylene triamine.

[1] The critical-PVC is the point where the binder no longer completely coats the pigments and micro-air voids form between the pigments.

The suspension was polymerised at 95°C for 3hours and then diluted in 4000.0 parts of water and allowed to settle. The concentrated sediment was removed as the product. The average particle size was found to be 15µm with vesicles comprising 25% by volume and size of less than 2µm.

2.2.1.2 Improved Particle Stability

Gunning et. al. (1972) observed that granules prepared by the above process were 'dimensionally unstable' and prone to shrinking whilst drying. This shrinking had an adverse effect on surface coatings, causing cracks to form when the vesiculated granules were present in sufficiently high concentrations. This prompted Gunning et. al. (1972) to develop and patent a process of preparing an aqueous slurry of vesiculated granules which did not suffer from shrinking and therefore was more suitable for use in coatings. Gunning et. al. (1972) described a typical example of preparing the vesiculated granules as follows:

An UPR was prepared from a 3:1:4.4 molar ratio of fumeric acid, phthalic anhydride and propylene glycol, respectively. The UPR was prepared as a 70% by mass solution in styrene with an acid value of 22mg KOH per gram UPR and a Gardner-Holdt viscosity of Z_3.

An aqueous mill-base was prepared by blending 208.0 parts titanium dioxide, 0.8 parts sodium hexametaphosphate and 104.0 parts water.

A water-in-oil emulsion was prepared by dispersing a mixture of 170 parts of the mill-base and 0.9 parts diethylene triamine into a mixture of 91.0 parts UPR, 45.5 parts styrene and 7.5 parts of a 50% by weight paste of benzoyl peroxide.

This emulsion was immediately stirred vigorously in an aqueous solution of 1.8 parts hydroxyl-ethyl cellulose, 6.8 parts 87-89% hydrolysed poly(vinyl acetate) and 409.4 parts water. Once the maximum droplet size was approximately 20µm the stirrer speed was reduced and 1.5 parts of diethylaniline was added.

The batch was allowed to exotherm during polymerisation. This resulted in granules less than 20µm in diameter with vesicles approximately 70% by volume and shrinkage of 4%. The shrinkage below 5% indicated that the granules could be considered to be 'dimensionally stable'.

2.2.1.3 Reduced Free Monomer

The Tioxide Group Ltd (1981) indicated that the processes for producing VP in the prior art resulted in incomplete polymerisation with high levels of free monomer and a pungent odour. The high levels of free monomer and the objectionable odour made the VP unsuitable for use in household aqueous coatings. The process patented by the Tioxide Group Ltd (1981) was experimentally determined to reduce the high free styrene content of 2.9% to as low as 0.2% for the patented process. Tioxide Group Ltd (1981) described a typical example of preparing the vesiculated particles as follows:

> An UPR was prepared from a 3:1:4.5 molar ratio of fumeric acid, phthalic anhydride and propylene glycol, respectively. The UPR was prepared as a 70% by mass solution in styrene with an acid value of 24mg KOH per gram UPR and a viscosity of 25poise.
>
> A water-in-oil emulsion was prepared by dispersing a mill-base (114 parts water, 20.5 parts 5% aqueous solution of Calgon PT®), 267 parts rutile TiO_2 pigment and 2.5 parts diethylene triamine into 309 parts of a 50% solution of UPR in styrene.
>
> A water-in-oil-in-water emulsion was prepared by adding 177 parts of the water-in-oil emulsion under high speed stirring to an aqueous phase (0.54parts hydroxy-ethyl cellulose, 2.55 parts of 90% hydrolysed poly(vinyl acetate) and 171 parts water).
>
> To the mixture 131 parts of 90°C water was added to produce an emulsion with a temperature of 46°C. Curing was initiated by the addition of 1.25 parts cumene hydroperoxide, 10 parts of a 2% aqueous solution of diethylene triamine and 2 parts of a 0.9% aqueous solution of ferrous sulphate.
>
> The mixture exothermed to 60°C after 2 hours and was left overnight to finish curing. This resulted in a VP product of an average diameter of 12µm and a free styrene content of 0.2%.

2.2.2 Commercialised Vesiculated Particles

2.2.2.1 Ropaque® Opaque Particles

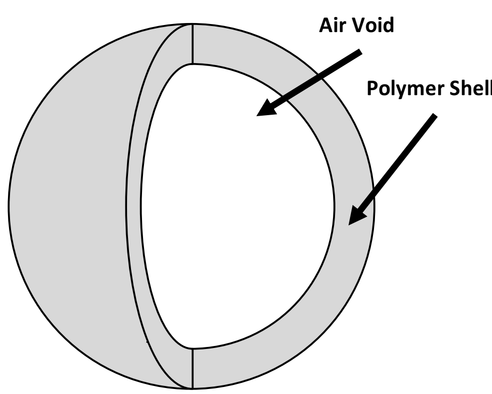
Ropaque® (Figure 2.1) is a single-void polystyrene polymer microsphere dispersion (Stewart, 1993). Upon drying the liquid in the polymer microspheres irreversibly diffuses through the shell and is replaced by air resulting in an opaque powder with no film forming capabilities. The difference between refractive index of the air and the polymeric shell significantly scatters light giving opacity to the particles making them suitable for the partial replacement of titanium dioxide pigments.

Ropaque® is manufactured by an emulsion polymerisation process to a particle size of approx. 0.4microns (Stewart, 1993) to maximize the spacing of titanium dioxide and making it suitable for gloss and sheen paints.

The particles are manufactured by sequential emulsion polymerisation in dispersed particles of which a core of a polymeric acid is encapsulated in a hard shell polymer (Martin & Kowalski, 1981). A volatile base (e.g. ammonia) diffuses to the core and reacts with the polymeric acid by hydrolysis. The polymeric acid swells creating micro cracks in the hard shell and the neutralised polymeric acid diffuses out producing an encapsulated micro-void. Ropaque® is recognisable as a milky white liquid.

The lower cost of Ropaque® compared to TiO_2 gives Ropaque® its distinct advantage of being able to reduce the paint formulation cost without sacrificing on the performance of the paint, however Ropaque® is not shear stable as a dispersion and therefore has the disadvantage of not being able to be incorporated into a grind (Dow Chemical Company, 2010).

Figure 2.1: Schematic of Ropaque® Opaque Particle.



2.2.2.2 Spindrift®

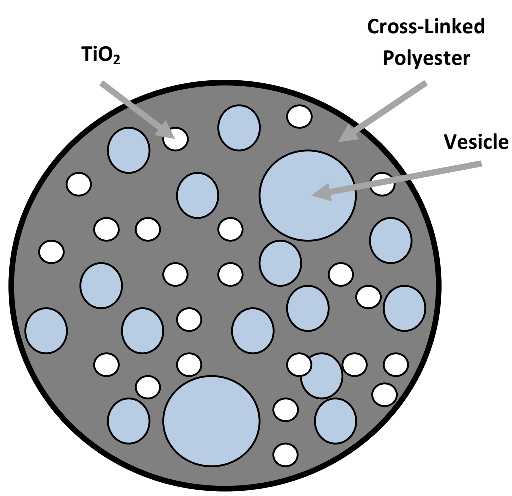
Spindrift® pigmented vesiculated beads (Figure 2.2), developed by Dulux Australia in the 1970's and commercialised in the 1980s (Ritchie, 1993) are spherical polymeric beads which contain multiple micro-voids and encapsulated titanium dioxide. Spindrift® is produced as a dispersion in a continuous aqueous phase, the micro-voids are filled with water and upon drying the water diffuses out of the beads giving the beads their opacity. The TiO_2 encapsulated in the beads adds to the opacity of the coating in both the wet and dry state (the micro-voids add no opacity to the paint in their wet state).

Spindrift® is produced by a double emulsification/ suspension polymerisation process (Ritchie, 1993). A first stable water-in-oil emulsion is formed when a mixture of dispersed TiO_2 in water, is dispersed into an organic mixture of UPR, copolymer monomer (styrene) and a polyamine (Gunning et. al., 1972). A second emulsion is formed by dispersing the organic phase into an aqueous colloid solution under constant agitation, forming a water-in-oil-in-water double emulsion. Finally, polymerisation is initiated when the beads have been determined to be of the desired size (Ritchie, 1993). The stable solid multi-vesiculated beads are formed by the cross-linking of the UPR with the styrene.

According to Gunning et. al. (1972), the vesicles are known to be vapour permeable but not normally permeable to liquids. Ideally the vesicles should not exceed one fifth of the diameter of the particle for sufficient opacity to be obtained. It is also desirable that the particles do not shrink appreciably upon drying as this can cause defects in the coating.

Due to the particle size (mean 5-12µm) of the Spindrift® beads they are only suitable for matt paints and in small quantities, for sheen paints (Ritchie, 1993).

Figure 2.2: Schematic of Spindrift® Pigmented Vesiculated Bead.



2.3 Multi-Vesiculated Particles (MVP)

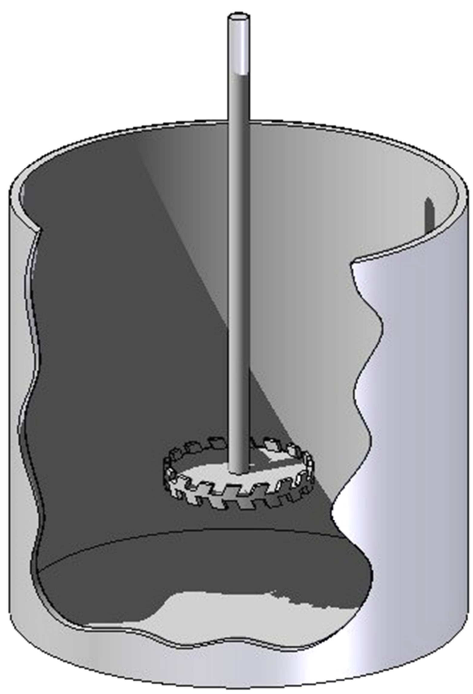
2.3.1 Description, Concerns and Product Specifications

Comex, (Based in Mexico) a member of the Nova Paint Club, started a research project to develop and commercialise a variation of MVP. Comex initially tried the double emulsification process, similar to the Spindrift® process, using a high-shear saw-tooth blade mixer (Figure 2.3), however due to difficulties with the scale-up of the process the project was terminated (Terblanche, 2002).

The technology was made available to the other NOVA Paint Club members of whom Plascon South Africa (Pty) Ltd continued the research and through a joint project with the Stellenbosch University was able to scale-up and commercialise a novel manufacturing process for the MVP.

The final MVP product patented by Plascon was designed for the partial replacement of titanium dioxide in paint manufactured by a process which exhibited effective control over the particle size distribution (Engelbrecht et al., 2006). The particles were spherical in shape with multiple air voids which hinder the re-entry of water once dry (Engelbrecht et al., 2006).

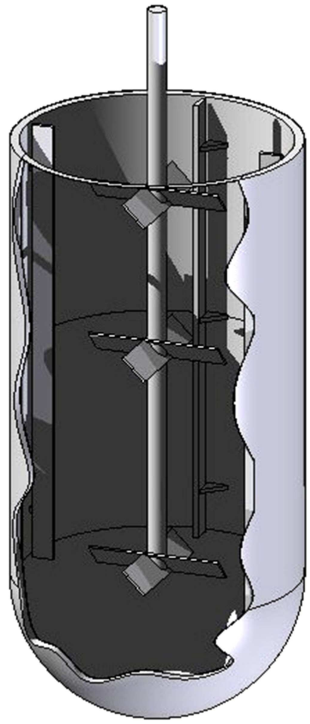
Figure 2.3: Saw-tooth Blade Mixer and Vessel.



The MVP are currently produced in a (four) baffled vessel using four 45° pitched turbine blades (3 turbines per shaft) depicted below (Figure 2.4) The pitched turbine blades apply a low-shear axial mixing which is significantly enhanced by the use of baffles in the reactor.

The process developed and patented by Plascon is based upon a mass suspension polymerisation system: The UPR is firstly prepared in a bulk polymerisation system before being added to the MVP reactor to form a suspension wherein the final polymerisation step takes place.

Figure 2.4: Batch Reactor used to produce the MVP.



The focus of this study is on the Suede effect MVP; the product is similar in nature to the Spindrift® product (described above) but with an average particle size distribution (SMD) of 20-30 microns (VMD=35-60µm) The Suede MVP are multi-vesiculated particles with a coarse textured appearance due to the size of the particles. The Suede effect in paint is obtained both from the method for which the paint is applied but more significantly from the contrast in appearance of the white opaque MVP against the coloured base paint (Figure 2.5). The coarse MVP particles become visible once dry and the MVP scatters light. The particle size is critical in obtaining the desired effect.

Figure 2.5: Suede Paint

The critical properties of the Suede MVP product are the products stability (resistance to settling and agglomeration), the effect on the tint strength of the final paint product (highly correlated with the variance of the PSD) and of most significance the particle size distribution (PSD), characterised using the Sauter-mean-diameter (SMD) and the Volume mean diameter (VMD). The Specifications for the Suede MVP are listed in Table 2.1.

Table 2.1: Specification of MVP Properties.[1]

Property	Specification
Non-volatile Content	23.5 – 24.5%
Viscosity (Brookfield LVT #3/30rpm)	2000-15000cP
pH	7.5-9.0
Particle Size (SMD)	20-30microns
Particle Size (VMD)[2]	35-60microns
Specific Gravity (wet)	1.040 – 1.050 kg/L
Stability	Slight Syneresis/ No Settling

In his thesis Terblanche (2002) highlighted several areas where a better understanding of and improvements to, the process could be made. Terblanche (2002) indicated that there was a lack of understanding of how the UPR affects the MVP particularly with regards to the most influential characteristics of the UPR. He also indicated that there was significant room to improve the process through modelling and optimisation of the process in the current reactor.

Gous (2003) suggested that a better understanding of the mechanism of vesicle formation and a method for quantifying vesiculation would be invaluable to optimising the MVP product and process. The exact mechanism of the formation of the vesicles is unknown (Terblanche, 2002) but a possible mechanism has been hypothesised as follows:

> A polyamine (DETA) is added to the UPR/styrene solution (organic phase) to partially neutralise the free carboxyl groups on the UPR (Terblanche, 2002) the amine groups orientate themselves in such a way as to produce micelles within the organic phase (Gous, 2003). During the dispersion of the organic phase within the aqueous phase, the aqueous phase migrates to the micelles within the organic phase and stable aqueous droplets form within the dispersed organic phase. As Gous (2003) determined the UPR/DETA has no affinity for water alone but only for the aqueous phase of the MVP process particularly due to the presence of the partially hydrolysed Poly(vinyl acetate).

[1] Technical Data Sheet: Multi-Vesiculated Particles (2008)
[2] Clarke (2009)

2.3.2 Suspension Polymerisation

Ullmann's Encyclopaedia of Industrial Chemistry (1992) describes suspension polymerisation as a series of processes which involves the dispersion and emulsification of insoluble monomer droplets in a continuous phase. A free radical initiator, usually soluble in the monomer phase, is used to initiate the reaction. A typical process involves water-insoluble monomers, containing an organic soluble initiator, being dispersed in a continuous aqueous phase by agitation and water soluble stabilisers. The continuous aqueous phase serves the dual purpose of, firstly assisting with the formation of the monomer droplets and then to stabilise the solid polymer particles. The dispersed monomer droplets are subjected to turbulent pressure fluctuations and viscous shear forces which break them into smaller droplets. The continuous collisions between the monomer droplets can result in coalescence of the particles (the stabilisers can prevent the coalescence of the particles). Under constant mixing conditions the monomer droplets will reach a dynamic equilibrium with a constant particle size distribution. The kinetics of the droplets/particles are in good agreement with those of bulk polymerisation provided the monomers are insoluble and mass transfer effects between the two phases can be ignored (Yuan et. al., 1991).

Yuan et. al. (1991) distinguishes between three types of suspension polymerisations:

1. Bead Suspension Polymerisation: The polymer is soluble in its monomer. During polymerisation the droplets pass through a viscous state with the final product being a suspension of solid clear spheres, e.g. expandable polystyrene.
2. Powder Suspension Polymerisation: The polymer is not soluble in its monomer which results in a bulk precipitation polymerisation in each droplet. The polymer forms opaque irregular grains, e.g. poly(vinyl chloride).
3. Mass Suspension Polymerisation: A two stage process in which the monomers are initially polymerised (low conversion) in a bulk polymerisation process and the viscous reaction mass is then suspended in an aqueous stabiliser solution, e.g. Acrylonitrile-Butadiene-Styrene resin.

All the above processes are either batch or semi-batch processes and Yuan et. al., (1991) indicated that at the time of publishing no commercial continuous suspension polymerisation process had been developed.

During the polymerisation reaction the dispersed phase transitions through various rheological stages. Jahanzad et. al. (2005) outlines four stages experienced during the polymerisation:

1. Transitional Stage: There is a higher rate of drop breakage than coalescence in this stage, which results in the exponential decrease of the drop size and the narrowing of the distribution of the droplets.
2. Quasi-Steady-State Stage: The breakage and coalescence rates of the droplets are approximately equal which results in a dynamic equilibrium of the particle size distribution.
3. Growth Stage: The drop breakage rate falls below the coalescence rate which results in the enlargement of the droplets and the broadening of the particle size distribution. It is often referred to as the "sticky stage'.
4. Identification Stage: The drops start to behave like solid particles and have a constant particle size and distribution. The particles no longer coalesce or break apart.

Vivaldo-Lima et. al. (1997) listed the following advantages and disadvantages for suspension polymerisation when compared with other polymerisation processes:

1. Advantages:
    - Ease of heat removal and temperature control due to the continuous phase.
    - Low dispersion viscosities, again due to the continuous phase.
    - Fewer impurities when compared with emulsion polymerisation.
2. Disadvantages:
    - Lower productivity due to long batch times and unavailability of a continuous process.
    - Waste water problems. This is only a problem when the polymer particles are to be separated from the continuous phase.
    - Polymer buildup on surfaces of the reactor during polymerisation.
    - No commercially available continuous processes.
    - Wide particle size distributions. This is of particular concern when a narrow PSD is a critical characteristic of the polymer particles.

The particle size distribution (PSD) is often considered to be a very significant characteristic of the polymer particles. The PSD is affected by geometric factors, operating parameters and physical characteristics of the reaction mixture. This is particularly true for the Suede MVP system and will be a focus for its optimisation.

2.3.3 Formulation

The formulation previously developed for the Suede MVP is represented in Table 2.2. A brief discussion of each component follows.

Table 2.2: Formulation

-	***Component***	***Percentage***
	Organic Phase	
1	Unsaturated Polyester Resin (UPR)	15.13%
2	Titanium Dioxide Pigment	0.88%
3	Styrene	5.78%
4	Lauryl Methacrylate (LMA)	0.68%
5	Diethylene Triamine (DETA)	0.21%
	Aqueous Phase	
6	Water	51.45%
7	PVOH Solution	13.13%
8	HEC Solution	10.34%
9	Diethylene Triamine (DETA)	0.06%
	Initiator System	
10	Water	0.21%
11	Ferrous Sulphate	0.01%
12	Cumene Hydroperoxide (CHP)	0.12%
	Post Treatments	
13	Surfactant	0.99%
14	Water	0.38%
15	Ammonia Solution	0.19%
17	HASE[1] Thickener	0.19%
18	Acticide	0.24%
	Total	100.00%

Unsaturated Polyester Resin (UPR)[2]

An unsaturated polyester resin-styrene solution (~68% Non-Volatile Components (NVC)) is used due to its carboxyl end-groups and un-reacted double bonds. The unsaturated carbons are needed to react with the styrene to create the cross-linked bead. The carboxyl end-groups are neutralised by the DETA which is crucial for the formation of the vesicles in the MVP.

Titanium Dioxide Pigment

The titanium dioxide pigment is added to the formulation to increase the opacity and whiteness of the MVP. The particles have poor wet opacity as a suspension and therefore the titanium dioxide pigment greatly enhances the wet opacity of the product.

[1] Hydrophobically Modified Alkali Swellable Emulsion.
[2] Refer to Chapter 2.3.5 for more detail.

Styrene

Styrene is a water insoluble unsaturated monomer and diluent for the UPR. Styrene easily copolymerises with the UPR to form the cross-linked polymer particle (Terblanche, 2002).

Lauryl Methacrylate (LMA)

The LMA is used to increase the hydrophobicity of the final polymeric bead which increases the water resistance of the particles (Engelbrecht et. al., 2006). The increased water resistance is a desirable characteristic of the MVP. The LMA has been shown to increase the particle size of the MVP.

Diethylene Triamine (DETA)

DETA is used to neutralise the carboxylic groups of the UPR and is critical to the formation of the vesicles as it is critical in the water up take of the organic phase (Gous, 2003). The DETA partially ionizes the UPR's carboxyl groups; this ion interaction causes the UPR molecules to orientate in the region of the DETA creating a more stable macro-molecule (Terblanche, 2002) for stable vesicle formation.

Water

Water is used primarily as the suspending agent (continuous phase) and is used to form the vesicles in the MVP. It is also critical to remove the heat generated during polymerisation and prevent a runaway reaction.

Hydrolysed Poly(vinyl Acetate) (PVOH) Solution

The PVOH solution is used to stabilise the droplets inhibiting the coalescence mechanism of the droplets (Yuan et. al., 1991). The PVOH solution affects both the stability of the suspension and the discreetness of the particles. In the final product the PVOH solution helps to prevent the settling of the solid particles in the suspension. PVOH has been observed to form a thin, gel-like layer around the monomer droplets which hinders coalescence of the droplets (Mikos et. al., 1986).

Work conducted by Koen (2004) and Gous (2003) indicate that the PVOH solution is critical for the formation of stable vesicles in the MVP.

Hydroxy Ethyl Cellulose Thickener Solution

The thickener is added to increase the viscosity of the aqueous phase. Its function is two-fold, firstly it affects the PSD of the particles since the PSD is affected by the viscosity (Yuan et. al., 1991) and secondly it prevents the settling of the solid particles in the final product.

Initiator System (Ferrous Sulphate & Cumene Hydroperoxide)

The initiation system consists of an organic peroxide initiator (cumene hydroperoxide) and metal Redox activator (Ferrous Sulphate) that acts as a catalyst so that free radical formation can occur at ambient temperature. The metal Redox activator is needed to reduce the radical formation temperature from 120°C to ambient temperature (Terblanche, 2002; Masson, 1989). The Redox activator reduces the peroxide group to form an anion and an oxygen-centred radical. The radicals react with the unsaturated carbon-carbon bonds of the UPR and styrene to create the solid cross-linked polymeric particles (Terblanche, 2002)

Surfactant

A surfactant is added to reduce the viscosity for further processing and to electro-statically stabilise the suspension (Terblanche, 2002). The surfactant prevents agglomeration of the particles and improves the processing and handling properties of the suspension.

Ammonia Solution

Ammonia is used to raise the pH of the suspension; the reasons are twofold, firstly the thickener used in the system is pH dependent and requires a pH of above 7.5 (Rohm & Haas, 2001). Secondly, a high pH enhances the product's resistance to bacterial contamination.

HASE Thickener

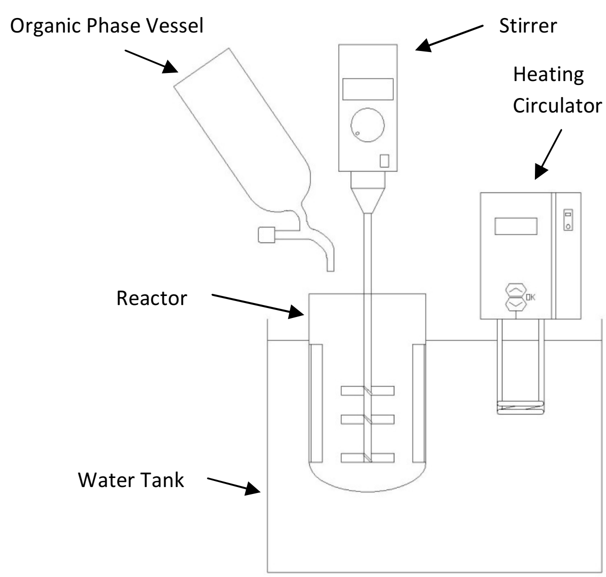
The HASE thickener is added to increase the viscosity and therefore stabilise the MVP to prevent settling of the particles during storage and transportation.

Acticide

An Acticide is added to prevent bacterial and fungal attack on the product and to increase the shelf life of the MVP.

2.3.4 Manufacturing Process

Figure 2.6: MVP Lab Reactor



The MVP process is done in a batch reactor under low shear conditions. The batch reactor used in the process (Figure 2.7) consists of a stirrer with 3 pitched (45°) turbine blades (4 blades per turbine) for low shear mixing which promote axial flow in the system. The reactor itself is a round-bottom vessel with 4 baffles to improve the mixing efficiency of the system. The reactor is jacketed (a water tank and heating circulator is used for simplifying the lab setup) to control the temperature and aid in increasing the temperature for curing the product.

Stage 1: Aqueous Phase Preparation

The aqueous phase is prepared by mixing the PVOH Solution, HEC Solution and Water in the Reactor under low speed stirring until a homogenous solution is attained. DETA is then charged to neutralise the system and to avoid a pH shock when the organic phase is added (Terblanche, 2002).

Stage 2: Organic Pre-Dispersion

The titanium dioxide pigment is dispersed in the UPR for approx 10minutes under high speed, high-shear conditions by a saw-tooth blade in a separate vessel (similar to Figure 2.3). The speed of the stirrer is reduced and the styrene and LMA monomers are mixed in the solution until homogenous. DETA is then added to the mixture and neutralisation takes place (a temperature increase is observed). The mixture needs to be used within 2 hours to avoid gelling of the organic phase.

Stage 3: Addition and Emulsification

The organic phase is added slowly at a constant rate to the aqueous phase under constant mixing for a period of 10 minutes. An emulsification period is then allowed for the droplets to reach the required particle size distribution (PSD) preferably at the dynamic equilibrium of the PSD.

Stage 4: Initiation

The ferrous sulphate is dissolved in water, added to the reactor and allowed to mix for 3 minutes. The CHP is then mixed in the reactor for a further 3 minutes. The stirrer is stopped at this point for 30 minutes as it is believed that this allows for absorption of the initiator into the organic phase (Gous, 2003).

Stage 5-6: Curing and Temperature Ramping

After the 30 minute stationary period the temperature is ramped to 50°C over 30minutes and held at 50°C for 1 hour to aid in curing the MVP. The temperature is then ramped to 60°C over 30minutes and held at 60°C for 3hours to reduce the free monomer in the product. The Reactor is then allowed to cool overnight (the batch is cooled immediately using the reactor jacket in the production plant.)

Stage 7: Post Treatment

The post treatment is then conducted. The components are added sequentially (as in Table 2.2) and allowed to mix for 10minutes each between additions.

2.3.5 Unsaturated Polyester Resin (UPR)

The UPR has been noted by several authors (Terblanche, 2002; Gous, 2003; Simpson, 2010) to have a significant impact on the properties of the MVP. This suggests that the formulation and process of the UPR as well as its final characteristics are critical to the control & optimisation of the MVP product characteristics.

In the patent of Gillian & Kershaw (1969), it was suggested that any UPR which meets their test requirements[1] should be suitable for forming vesiculated granules. However, the patent (Gillian & Kershaw, 1969) did suggest that the UPR should be produced from a α,β-ethylenically unsaturated acid in combination with a saturated acid or anhydride and a suitable dihydric alcohol. An example from the patent (Gillian & Kershaw, 1969) indicates that a typical UPR would be produced from a 3:1:4 molar ratio of fumeric acid, phthalic anhydride and propylene glycol, respectively. The UPR should be diluted in xylene (70% by mass UPR) and have an acid value of between 5 – 75mg KOH per gram UPR (preferably 10-50mg KOH/g) and a Gardner-Holdt viscosity greater than E (preferably greater than S).

In the patent of Gunning et. al. (1972) the dimensional stability of the vesiculated granules of Gillian & Kershaw (1969) were questioned and they proposed several improvements to the process, including the UPR. Gunning et. al. (1972) indicated that styrene was the preferred diluent for the UPR and that a preferred acid value range of 17-25mg KOH per gram UPR would improve the dimensional stability of the vesiculated granules. The use of styrene as a diluent and the reduced acid value range was used by many of the subsequent patents (Tioxide Group Ltd, 1981; Goldsbrough & Hodge, 1983; Karickhoff, 1984; Engelbrecht et. al., 2006) as the preferred characteristics for the UPR.

The UPR utilized by Engelbrecht et. al. (2006) had the following composition:

1)	Propylene glycol	30.35%
2)	Phthalic anhydride	12.96%
3)	Maleic anhydride	25.75%
4)	Styrene	30.75%
5)	Inhibitor (10% Soln.)	0.18%

The primary UPR reaction is represented in Figure 2.. The UPR can be produced in the lab by heating components 1-3 under a blanket of nitrogen to 120°C and allowing the temperature to reach its peak exotherm. The mixture is then heated to between 200-260°C and the water condensate is removed. The reaction is allowed to proceed until the required acid value and viscosity have been achieved. The UPR is then slowly added to the styrene and inhibitor ensuring that the temperature never exceeds 60°C. (A more detailed laboratory process is described in Appendix B). Typical specifications of the UPR used to manufacture the Suede MVP are listed in Table 2.3.

[1] (Refer to Chapter 2.2.1.1 or the patent (Gillian & Kershaw, 1969))

Figure 2.7: Formation of the UPR.

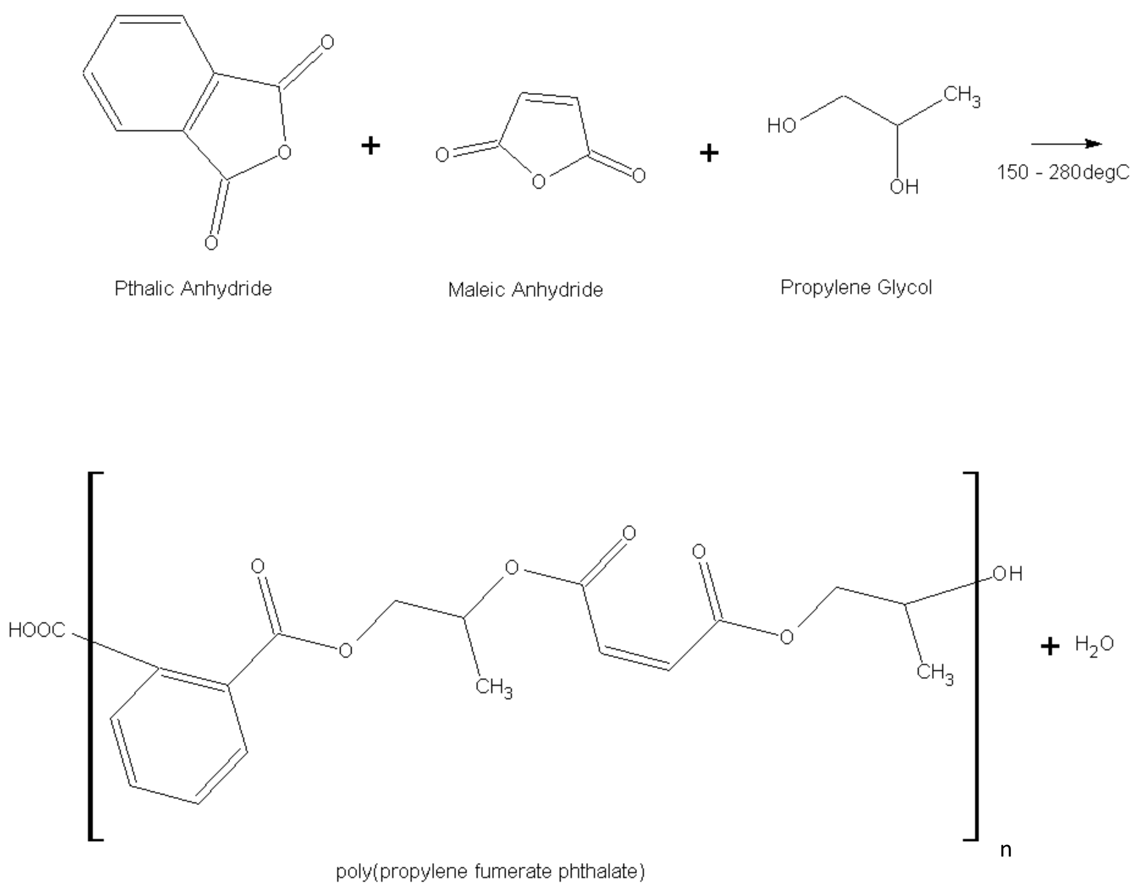


Table 2.3: Typical UPR Specifications[1]

Acid value (on solid) /mg KOH/g	24 – 28
Non-volatile content /%	66 - 68
Viscosity @ 25°c, Gardner–Holdt	T - U
Liquid appearance	clear
Relative density @ 25°C	1.09 – 1.13
Time to gel[2] /mins	40 – 55
Cure time /mins	50 – 65
Peak exotherm /°C	178 - 185

[1] Terblanche (2002).

[2] Curing characteristics @ 25°C, (100g resin, 0.5g AC-2, 2g Butanox M-50)

2.4 Modelling

"All models are wrong, but some are useful"

- G.E.P. Box (Carlson & Carlson, 2005)

Mathematical models explain patterns and trends from observations or experiments (controlled observations). Dobre & Sanchez-Marcano (2007) define a model as the 'description of phenomena, as a collection of empirical and theoretical equations that can both explain and predict the phenomena'. A Model is nothing more than a simplification of complex real world phenomena that is simplified to a level which can be comprehended and computed, based on assumptions made through a scientific understanding of the world. For example the Laws of Nature are nothing other than generalised models based upon our scientific knowledge of the universe.

Luyben (1990) stated that the most important result of developing a model is to gain an understanding of the core of the process, to strip away the extraneous factors of the system and to reveal the critical variables which affect the system.

The general model building process, as described by Edgar et. al. (2001), is conducted over three stages:

1. Problem definition and formulation – The problem is defined and important elements of the problem and its possible solution are identified.
2. Preliminary and detailed analysis (design phase) – Develop mathematical description of the model and estimate parameters (based on physical-chemical knowledge or experimental results).
3. Evaluation phase – evaluate and verify the developed model under controlled conditions to determine its accuracy and validity.

There is a multitude of different ways of classifying models based upon different criteria. Often models are divided into two broad categories, (1) Phenomenological and (2) Empirical models. (1) Phenomenological models are based on the system's phenomena/mechanisms/fundamental laws such as the continuity equation (mass balance), energy equation, equations of motion, transportation phenomena, equations of state, equilibrium and chemical kinetics (Luyben, 1990). (2) Empirical models follow an input-output approach based on experiments or observations with equation fitting regression for parameters with no physical meaning (Hangos & Cameron, 2001).

Carlson & Carlson (2005) divided models into three categories, Hard models (e.g. Thermodynamic Models) Soft Models (e.g. Empirical models) and Local Models (e.g. Response Surface Models). Hard models are generally deduced from defined laws or theories following fixed mathematical structures for which the parameters are known or derived from theoretical means. For example the generalised kinetic rate equation:

$$\frac{d[product]}{dt} = k(T)[A]^a[B]^b[C]^c \cdots [Z]^z \tag{2.1}$$

Soft models are generally developed from empirical or experimental data and a model is regressed from the observed relationship between the dependent and independent variables:

$$y = f(x_1, x_2, \ldots, x_k) + \varepsilon \tag{2.2}$$

Local models are soft models fitted for data over a small subsection of the available experimental space. They are usually used for optimising a process for a subset of critical parameters.

Dobre & Sanchez Marcano (2007) used the theoretical basis of the model as the classification criterion; the following classes emerged:

1. Mathematical models based on the laws of transport phenomena (Deterministic).
2. Mathematical models based on the stochastic evolution laws.
3. Mathematical models based on statistical regression theory.
4. Mathematical models resulting from the particularisation of similitude and dimensional analysis.

Regardless of how the model is to be classified the following decisions need to be made to choose the right model for the right application:

1. How the model is to be developed fundamentally, empirically or a combination of both?
2. How accurate the model needs to be?
3. What resources are available for the model development?

Once these questions have been answered the model can begin to be developed.

2.4.1 Phenomenological

Phenomenological models are based upon physical phenomena (e.g. mass, heat and momentum transfer), known mechanisms (e.g. Chemical reaction rates) and fundamental laws (e.g. conservation of mass and energy). The models are considered to be hard since the relationship between the input and output variables have been determined by a theoretical understanding of the system. If the parameters of the system are known it is possible to predict the output from the input by solving either analytically or numerically the model equations. In principle, if the initial conditions and physical phenomena of a system are known a hard model should be able to accurately predict the outcome of the system analytically (Carlson & Carlson, 2005). In contrast for a soft model the dependent and independent variables are observed and a function is fitted to the data by regression.

A few suspension polymerisation systems have been successfully modelled using Population Balance Equations (PBE) to model and predict the particle size distribution. The formation of particle size distribution has been modelled by many researchers (Alvarez et. al, 1992; Kiparissides, 2006; Chen et. al., 1999 – to name a few) using PBEs by the phenomena of breakage and coalescence of the droplets during processing. One general form of the equation is given by Kotoulas & Kiparissides (2006) as follows:

$$\frac{\partial[n(V,t)]}{\partial t} = \int_{V}^{V_{max}} \beta(U,V)u(U)g(U)n(U,t)dU + \int_{V_{min}}^{V/2} k(V-U,U)n(V-U,t)n(U,t)dU$$
$$-n(V,t)g(V) - n(V,t)\int_{V_{min}}^{V_{max}} k(V,U)n(U,t)dU \qquad (2.3)$$

$n(V,t)$ is the number density function describing the particle size distribution. The first term on the right-hand-side (r.h.s.) of the equation represents the generation of droplets due to breakage within the range (V – V+dV), where $\beta(U,V)$ is the daughter droplet breakage function, $u(U)$ is the number of daughter droplets formed from a drop of size U and $g(U)$ is the breakage rate of drops of volume

U. The second term represents the generation of droplets due to coalescence of smaller droplets where $k(V-U,U)$ is the coalescence of 2 droplets of volume V & U. The third term is the droplet disappearance rate due to breakage and the fourth is disappearance due to coalescence (Kotoulas & Kiparissides, 2006).

Breakage and coalescence in industrial polymerisation occur in the inertial sub-range and therefore primarily occur due to turbulent velocity fluctuations and are independent of the main flow (Shinnar, 1961). Alvarez et. al. (1992) expressed the breakage and coalescence rates in terms of frequency and Maxwellian efficiency functions:

$$g(V) = \omega_b(V)e^{-\lambda_b(V)} \tag{2.4a}$$

$$k(V,U) = \omega_c(V,U)e^{-\lambda_c(V,U)} \tag{2.4b}$$

Alvarez et. al. (1992) went further to develop the functions $\omega_b(V)$, $\lambda_b(V)$, $\omega_c(V,U)$ and $\lambda_c(V,U)$ from a phenomenological basis.

Phenomenological modelling of suspension polymerisation using PBEs appears in the literature in various forms such as Vivaldo-Lima et. al (1998a) and Maggioris et. al (2000) who takes into consideration the non-homogenous nature of the mixing and applies the PBE to multi-zoned compartmentalised mixing models. Other researchers such as Chatzi et. al (1989) and Chatzi & Kiparissides (1992) manipulated the $u(U)$ and breakage function to obtain modelled bimodal distributions which represent the real particle size distribution of experimental batches.

The modelling of suspension polymerisation processes is a complex problem due to the highly coupled nature of the kinetics, thermodynamics, and heat & mass transfer phenomena in this heterogeneous system (Kiparissides, 2006). Unfortunately due to the complex nature of the multi-phase emulsion suspension polymerisation process used to manufacture the MVP a phenomenological model is not practical and therefore beyond the scope of this thesis.

2.4.2 Empirical

Not all engineering problems can be solved by phenomenological models either due to the complexity of the mathematics making it unfeasible or because the mechanisms of the process are not known. The alternative to using these methods is to fit a model to experimental data often in combination with a theoretical analysis of the system (semi-empirical models). One approach is to use dimensional analysis and similitude to model the data semi-empirically and to relate similar systems to each other or alternatively use statistical regression on the experimental data and develop a soft model for the data.

2.4.2.1 Dimensional Analysis

> "Dimensional analysis is based upon the recognition that a mathematical formulation of a chemical or physical technological problem can be of general validity only if it is *dimensionally homogenous"*
>
> - Marko Zlokarnik (2006)

Dimensional analysis models experimental data based upon dimensionally homogenous data sets of physical properties and characteristics of a system. The most common form for the modelling of experimental data using dimensional analysis is to create dimensionless groups and determine the mathematical relationship between the dependent dimensionless groups as a function of the independent dimensionless groups.

The Buckingham-Π method is a method for taking a dimensionally homogenous system of (n) parameters and reducing it to a smaller set of (n-m) dimensionless groups for analysis, where (m) is the number of dimensions (e.g. length or mass). These dimensionless (semi-)empirical models in conjunction with the principles of similitude are readily useable for the scaling-up or scaling-down of processes.

Dimensional analysis has successfully been used to develop dimensionless equations and in conjunction with the principles of similitude these equations have been used for scale-up of suspension polymerisation reactors (Langner et. al., 1980). Langner et. al. (1980) went further to propose the following general dimensional equation for suspension polymerisations:

$$^{d_p}/_{D} = kRe^a We^b Ne^e \left(^{\rho_d}/_{\rho_c}\right)^f \left(^{\mu_d}/_{\mu_c}\right)^g \phi^h \tag{2.5}$$

Yuan et. al (1991) lists more than 30 investigators with over 50 dimensional analysis empirical models for predicting average droplet diameter for a multitude of liquid-liquid dispersion systems. A common thread throughout these investigators work is the dependence of the particle size on the Reynolds and Weber numbers. The models are however very limited in application and are only applicable to specific geometries of reactors and chemical systems. For example Shinnar & Church (1960) have the following model which is only applicable in coalescence dominant systems:

$$^{d_{p_{min}}}/_{D} = K' \left(\frac{A(h)}{D\sigma}\right)^{3/8} We^{-3/8} \tag{2.6}$$

Or Hopff et. al. (1964) whose system is only applicable to MMA suspension polymerisation with PVA stabilizer:

$$^{d_{p_{50}}}/_{D} = KRe^{1/2} We^{-1} \left(\frac{\mu_d}{\mu_c}\right)^{0.1} \tag{2.7}$$

Arai et. al. (1977) developed a model for systems with a viscous dispersed phase which is dependent on the reactor scale:

$$^{d_{p_{max}}}/_{D} = K \left(\frac{\rho_c N d_r^2}{\mu D}\right)^{-0.75} \tag{2.8}$$

Chatzi et. al (1989) reported a generalized correlation model, in the form of equation 2.9. The equation was used to predict the Sauter-mean Diameter (d_{32}) for a range of experiments with very good results, however the equation was only applied to systems of very low (0.01-0.03) holdup ratio, ϕ, and therefore is not applicable to the MVP system.

$$d_{32}/_D = a(1 + b\phi)(We_T)^{-c} \tag{2.9}$$

Where c is often considered to be 0.6.

Since the dimensionless models are system specific, particularly with regards to the model parameters a new model will need to be developed for the unique MVP system (**Chapter 6**).

2.4.2.2 Statistical Models

Models based on statistical methods are useful when transport phenomena or stochastic method models are not available or poorly understood. Statistical models are useful for evaluating the relationship between process measurements without having a phenomenological understanding of the relationships. Statistical modelling is usually applied under 3 different circumstances (Dobre & Sanchez-Marcano, 2007):

1. The information on the process is incomplete and therefore a deterministic model cannot be developed.
2. The investigated model displays multiple complex states and therefore any deterministic model will be very complex.
3. The researcher's ability to develop a deterministic or stochastic model is limited.

It is recommended that statistical models be developed through designed experiments to maximise their accuracy and validity to the process. According to Dobre & Sanchez-Marcano (2007) the main advantages of using a statistical model are:

1. The model only requires the inputs and outputs of the process.
2. The model is verifiable as long as it has an experimental basis.
3. Strongly recommended for optimisation because of the mathematical expression basis and being verifiable models.
4. Complex models such as artificial neural networks are available for modelling dynamic processes.

Statistical models are based upon the Taylor expansion in the form of equation 2.10 (Dobre & Sanchez-Marcano, 2007) but in practice a simplified model such as equation 2.11 (first order) or 2.12 (second order) is preferred.

$$y_i = y_{i0} + \sum_{j=1}^{N}\left(\frac{\partial f_i}{\partial x_j}\right)_0 (x_j - x_{j0}) - \frac{1}{2!}\sum_{j=1}^{N}\sum_{k\neq j}^{N}\left(\frac{\partial^2 f_i}{\partial x_j \partial x_k}\right)_0 (x_j - x_{j0})(x_k - x_{k0})$$

$$-\frac{1}{2!}\sum_{j=1}^{N}\left(\frac{\partial^2 f_i}{\partial x_j^2}\right)_0 (x_j - x_{j0})^2$$

$$+\frac{1}{3!}\sum_{j=1}^{N}\sum_{k=1,k\neq j}^{N}\sum_{l=1,l\neq j,l\neq k}^{N}\left(\frac{\partial^3 f_i}{\partial x_j \partial x_k \partial x_l}\right)(x_j - x_{j0})(x_k - x_{k0})(x_l - x_{l0})$$

$$+\frac{1}{3!}\sum_{j=1}^{N}\sum_{k=1,k\neq j}^{N}\left(\frac{\partial^3 f_i}{\partial x_j^2 \partial x_k}\right)(x_j - x_{j0})^2(x_k - x_{k0}) + \frac{1}{3!}\sum_{j=1}^{N}\left(\frac{\partial^3 f_i}{\partial x_j^3}\right)(x_j - x_{j0})^3$$

$$-\frac{1}{4!}\sum_{j=1}^{N}\sum_{k=1,k\neq j}^{N}\sum_{l=1,l\neq j,k}^{N}\sum_{m=1,m\neq j,k,l}^{N}\left(\frac{\partial^4 f_i}{\partial x_j \partial x_k \partial x_l \partial x_m}\right)(x_j - x_{j0})(x_k - x_{k0})(x_l - x_{l0})(x_m - x_{m0}) + \cdots \tag{2.10}$$

Models are more commonly fitted empirically to a general first order linear equation of the form:

$$y = \beta_0 + \sum_{i=1} \beta_i x_i + \varepsilon \tag{2.11}$$

Or the second order equation commonly used for optimisation:

$$y = \beta_0 + \sum_{i=1} \beta_i x_i + \sum_{i,j} \beta_{ij} x_i x_j + \sum_{i=1} \beta_i x_i^2 + \varepsilon \tag{2.12}$$

For more advanced non-linear responses, neural networks can be more suitable.

A group of methods, known as Design of Experiments (DoE), has been frequently used, in the literature, to develop empirical models for suspension polymerisation systems using a variety of techniques and experimental design layouts. For example Romo et. al (2006) used a Res IV $2^{6\text{-}2}$ fractional factorial to study and optimize the suspension polymerisation of β-cyclodextrin and epichlorohydrin. They claim to have achieved a model for the selection of the optimal polymerisation conditions to create a polymer with specific properties. Arayapranee et al. (2006) used a $2_{IV}^{6\text{-}2}$ fractional factorial to study the influence of various process variables on the graft copolymerisation of styrene and methyl methacrylate onto styrene-butadiene rubber. Pourmehr & Navarchian (2009) used an L_{18} Taguchi orthogonal array to study the influence of 5 factors at 3-levels on the particle size distribution of the emulsion polymerisation of vinyl chloride. Mishra et al. (2009) used a $2_{IV}^{6\text{-}2}$ fractional factorial experiment to study the semi-continuous emulsion polymerisation of methyl methacrylate to obtain more useful and detailed information about the process than can be gained from one-factor-at-a-time (OFAT) experimental approaches.

Martin & Cuellar (2004) used a $2_{IV}^{8\text{-}3}$ fractional factorial DoE to empirically model the responses to optimise their product by maximizing the yield, & polymeric layer thickness and minimize particle agglomeration for the synthesized micro beads consisting of a stainless steel nucleus covered by a polymeric layer of poly(styrene-co-divinylbenzene). They were attempting to make magnetic resin micro-beads using suspension polymerisation. The 8 factors studied were as follows: double polymerisation (categoric), temperature, stirring speed, hold-up, %cross-linker, quantity of ammonia hydroxide, pre-polymerisation (categoric) and initiator-metal contact (categoric). These factors were chosen from a long list of possible factors that were ignored due to initial experimental trial results and literature review of previous work conducted in the field. The factor levels were determined the same way. An empirical model in the form of equation 2.12 was developed for the significant linear and 2-factor interaction effects only, for all the responses. The models were then used to optimise the global yield response.

Lucchesi et. al. (2007) used a fractional factorial DoE to optimise the suspension polymerisation of styrene, divinylbenzene & N-(p-vinylbenzyl)-4,4-dimethylazlactone (VBM), for a set of six factors. They used the L_{12} Plackett-Burman screening experimental design layout to screen 10 factors fitting the experiments to an empirical linear model in the form of equation 2.11. The factor levels were then set to maximize the responses according to the empirically modelled equation. A subset of 5 factors from the screening experiment as well as an additional factor (total of 6 factors) were then subjected to further experimentation using a 2^{6-3} fractional factorial DoE for optimisation. The problem with the approach used was that interaction effects were ignored (the authors indicated that this was of concern) and that no terms were included for the possibility of non-linearity in the response (The authors acknowledged in their concluding remarks that a response surface design would be more suitable for optimising the process). The authors used a desirability function to optimise this multi-response problem. The optimized factor levels were tested and validated.

Shahbazian et. al. (2009) used a Taguchi L_{18} orthogonal array of 5 factors at 3 levels to determine the effects of these factors on the batch emulsion polymerisation of vinyl chloride. The Taguchi L_{18} orthogonal array is a saturated Res III design and is best suited for a design with either 7 factors at 3 levels and 1 factor at 2 levels or 6 factors at 3 levels and 2 factors at 2 levels. Since the design can only be used to determine main effects a Res III 2^{5-2} fractional factorial of 8 experiments would have given the same results or rather a Res V 2^{5-1} fractional factorial with 16 experimental runs would have yielded more valuable 2-factor interaction effects for fewer experiments. The authors tried to reduce the number of experiments form an OFAT experimental method which would have only required a maximum of 15 (preferably 11) experiments which would have still resulted in the same information being obtained for a lower experimental cost. The authors acknowledged that the model was insufficient for optimisation and better suited for screening significant variables and that more experimental runs would be required to optimise the process. However an attempt at finding the relative optimum based on these experimental results was conducted using an overall evaluation criterion as suggested by Boieshan (1990).

More advanced DoE techniques are available and have been applied to suspension polymerisation systems such as Vivaldo-Lima et al (2006), who used a Bayesian experimental design technique to determine the relative importance of process factors in the particle size distribution of a suspension polymerisation and Vivaldo-Lima et al (1998b) who used a mechanistic model-based experimental design technique to determine polymerisation conditions and polymer properties for the suspension copolymerisation of styrene and divinylbenzene. Vivaldo-Lima et al (1998b) further went on to demonstrate that this technique was more adequate than other designed experimental techniques and used the results to determine the polymerisation conditions that could be used for the particle formation phenomena of their suspension polymerisation system.

2.4.3 Previous Modelling of MVP

Terblanche (2002) modelled the MVP system in a Saw-tooth blade vessel (Figure 2.3) using a dimensional model based upon the simplified model (equation 2.13) developed by Klein & Lowry (*sinne anno*) for emulsion polymerisation scale-up.

$$D_i^{0.765} N_{min} = k \tag{2.13}$$

Terblanche (2002) assumed the particle size α_t could be described by the constant term of equation 2.13, it was also determined that the particle size was a function of the impeller to vessel diameter ratio (D_i/d_t), and the emulsification time (t_e) resulting in equation 2.14:

$$\alpha_t^{-1} = 0.0448 N^{0.90} D_i^{0.52} \left({}^{D_i}/_{d_t}\right)^{0.44} t_e^{0.23} \tag{2.14}$$

The model was developed using a 5L and 20L vessel. Experiments were conducted on a 150kg scale vessel and compared to the empirical model results. It was found that the model predicted results compared well to the experimental data and that the model was more accurate for impeller to vessel ratios that were close to the 5L and 20L scale experiments.

Experiments were conducted both on the lab and industrial scale for an alternative formulation of MVP using additional surfactant, ignoring the effect of emulsification time Terblanche (2002) developed an empirical model (equation 2.15) which compared well to the experimental results.

$$\alpha_t^{-1} = 0.63 N^{0.76} D_i^{0.58} \left({}^{D_i}/_{d_t}\right)^{1.01} \tag{2.15}$$

Unfortunately the model developed by Terblanche (2002) was developed for a Saw-tooth blade mixer and is therefore not applicable for the Low-shear batch reactor used for the work in this thesis due to the violation of the assumption of geometric similarity.

2.5 Nomenclature

Latin Variable	**Description**	**Units**
A(h)	Energy of adhesion	unspecified
a, b, e, f, g, h, k, K, K'	Empirical model coefficients	-
D	Characteristic diameter	m
d	Diameter	m
f()	Function	-
$g(U)$	Breakage rate of drops	-
$k(V-U,U)$	Coalescence of 2 droplets	-
N	Impeller speed	s^{-1}
$n(V,t)$	Number density function	-
Ne	Newton number	-
Re	Reynolds number	-
t	Time	S
$u(U)$	Number of daughter droplets	-
U	Droplet volume	unspecified
V	Droplet volume	unspecified
We	Weber number	-
x	Independent variable	-
y	Dependant variable	-
Greek Variables	**Description**	**Units**
α	Particle size	m or μm
β	Statistical model coefficient	-
$\beta(U,V)$	Daughter droplet breakage function	-
ε	Error	unspecified
λ	Efficiency argument	-
μ	Viscosity	Pa.s
ρ	Density	$kg.m^{-3}$
σ	Interfacial tension	$kg.s^{-2}$
ϕ	Hold-up ratio	-
ω	Frequency	-

Subscript	**Description**	**Subscript**	**Description**
0	Mean	32	Sauter-mean
50	50^{th} Percentile	B	Breakage
c	Coalescence	C	Continuous
d	Dispersed	E	Emulsification
i, j, k, l, m	Generic reference	Max	Maximum
p	Particle	R	Reactor
T	Turbulent		

3 Experimental Methods & Analytical Techniques

3.1 Introduction

The batch suspension polymerisation, in a low shear turbine blade reactor of the multi-vesiculated particles has been studied by various authors (Terblanche, 2002; Fourie, 2008; Moolman, 2003; Gous, 2003). These authors focused on the development, scale-up and characterisation of the MVP with very little emphasis on the optimisation of the process and/or product. This is particularly true for the coarse textured effect MVP. Therefore there is the possibility for significant improvement of the process and the product through correct optimisation techniques.

The product also suffers from significant sensitivity to the batch-to-batch variation of the UPR raw material (Terblanche, 2002; Gous, 2003). Therefore when optimising the process care should be taken to ensure that the process is as robust to the UPR batch-to-batch variation as possible.

There is currently very little phenomenological knowledge of the current suspension polymerisation process for the manufacturing of multi-vesiculated particles and therefore a modelling and optimisation approach which does not require any phenomenological understanding of the process is desirable. Statistical modelling (Dobre & Sanchez-Marcano, 2007) and Design of Experiments (Montgomery, 2005) are well suited for this type of process modelling and optimisation problem and therefore forms an integral part of this thesis.

3.2 Design of Experiment

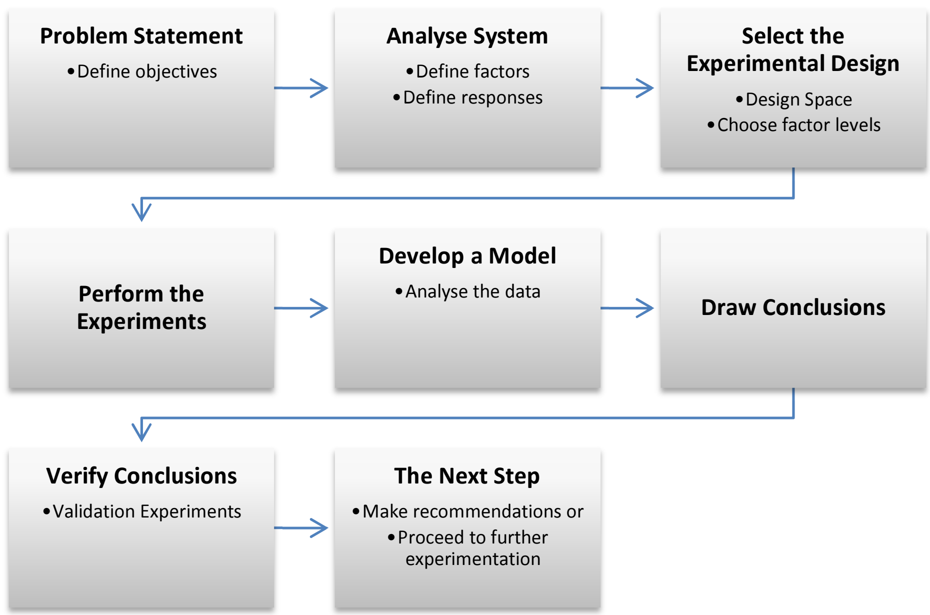
Design - **noun 1**: A **plan** or drawing produced to show the look and function or workings of something **before** it is built or made.

Experiment - **noun 1:** A **scientific procedure** undertaken to make a discovery, test a hypothesis, or demonstrate a known fact. **2:** a course of action tentatively adopted **without** being sure of the **outcome.**

(*Compact Oxford English Dictionary of Current English*, 2008)

Design of Experiments (DoE) is a set of tools and methods for extracting the maximum valuable information from a minimum set of experiments. Specifically the DoE process involves planning, designing, execution and analysis of the experiments following the general method illustrated in Figure 3.1. A well designed experiment is of extreme importance because the results and conclusions drawn depend largely on the manner in which the data was collected (Montgomery, 2005).

Figure 3.1: Design of Experiments.



The statistical analysis and modelling used on the designed experimental data allow for the unbiased drawing of the following types of conclusions (Montgomery, 2005):

1. Determine which variables are most influential on the response.

2. The levels that the independent variables need to span, to achieve the desired response.

3. Determining the levels of the independent variables to reduce the variability in the response variables.

4. At what levels the influential independent variables should be set to minimise the influence of the noise (uncontrolled) variables.

Various Strategies of experimental approaches have been used in practice:

1. Best-Guess Approach – the best levels of each factor are assumed based upon technical or theoretical knowledge and practical experience. This suffers from two problems; firstly a better solution may never be found and secondly if an improvement is obtained the experiment could stop with this suboptimal result (Montgomery, 2005).

2. One-Factor-at-a-Time (OFAT) - A baseline is chosen for each variable and then each variable is varied one at a time across its range of levels and then the optimum level for each variable is chosen independently. The main disadvantage of this approach is that it ignores variable interaction which can have a serious negative effect on the response (Montgomery, 2005).

3. Factorial – A factorial experiment has the form of $x^a y^b z^c$… where x, y & z are the levels of each factor and a, b & c are the number of factors which have x, y & z levels respectively. The number of experiments per replicate for these design is (x^a)*(y^b)*(z^c) (e.g. $2^5 3^4 4^1$=10368 experimental runs). The most common type of factorial design is a 2-level factorial of the form 2^x. This design has the advantage that all interactions are considered but has the

disadvantage that the total number of experiments increases exponentially with each additional factor (Montgomery, 2005).

4. Fractional Factorial – Fractional factorial experiments, the most common being the 2-level fractional factorial has the form 2^{x-y}. x represents the number of factors and y represents the fractional level (e.g. 1 = half fraction, 2 = quarter fraction, 7 = 1/128 fraction). The advantages of a fractional factorial design are that they require significantly fewer experimental runs especially for experiments with a large number of factors and are therefore well suited for screening experiments (Montgomery, 2005). However fractional factorials suffer from aliasing of the factor effects which can be a problem particularly for low resolution designs when important effects and their interactions are aliased and the influential factor cannot be determined. It is useful for fractional factorial designs to be referred to by their resolution which indicates the aliasing structure of the design.

5. Taguchi Orthogonal Arrays (OA) – in the 1950s and 1960s Dr. G. Taguchi revolutionised quality engineering through his unique take on quality as well as through his original experimental designs known as orthogonal arrays (Lochner & Matar, 1990). His methodology was brought to America in the 1980s where it became a popular method of quality design (Rekab & Shaikh, 2005). The Orthogonal Arrays are generally saturated resolution III designs[1] which suffer from complex aliasing structures. Whilst many statisticians are critical of his designs and recommend highly fractionated fractional factorials as alternative designs; Taguchi's OA designs are still regularly used in industry.

6. Response Surface Methodology (RSM) – RSM is a set of mathematical and statistical techniques used for the analysis of problems for which the response can be modelled as a surface (Montgomery, 2005). Thus there are many types of designs which fall under the subject and are chosen depending on the application of RSM. The most common are the Central Composite Design which can be added to experimental data gained form fractional factorials or the D-Optimal design which is commonly used for irregular/constrained design spaces. Other available designs are the Box-Behnken, Distance Based, Hybrid, Mixture, Alphabetic Optimal as well as many other designs all with their own strengths and weaknesses. (Refer to *Response Surface Methodology* by Myers et. al. (2009) for more details.)

3.2.1 Screening Designs

Screening (DoE) -

> 'Sifting through a large number of factors with the fewest number of experiments.'

The screening process is used to identify the factors with the most significant influence on the response variable for the minimum cost (quantity of experiments). Screening DoE commonly use

[1] Res III designs - main effects are confounded with 2-factor interactions.

highly fractionated factorial experiments with several centre points to determine the significant factors and if any curvature in the values exists.

Due to the exponential relationship between the number of experiments and the number of factors it is desirable to screen the factors at the lowest cost to determine the influential factors before any further experimentation takes place. For example if 16 factors were initially tested with only 5 of them being influential the two scenarios for optimisation are as follows:

- RSM optimisation design of 16 variables using a Box-Behnken Design (BBD): 268 experiments would be required.
- If a 2^{16-11} fractional factorial screening design was carried out followed by a BBD on only the 5 significant factors: 32 + 46 = 78 experiments would be required.

This is a reduction of approximately 71% in cost. Thus screening designs allow you to:

1. Determine the influential factors.
2. Determine any curvature in the response (if centre points are used).
3. Minimize the overall experimental costs (the saving increases exponentially as the number of factors increases).
4. It is a useful tool in determining the next phase of the experimentation.

Screening designs estimate linear models only and therefore tend to suffer from the drawback of being unable to estimate interaction effects. The general assumption used for screening experiments when moving to the optimisation stage is that any interaction effects involving non-influential factors will not be influential either (Montgomery, 2005). This is generally a safe assumption but care must be taken by the experimenter to confirm this result i.e. if from theory or experience a non-influential factors interaction is significant it should be incorporated in further experimental designs.

The successful use of fractional factorials is based on the following 3 ideas (Montgomery, 2005):

1. The scarcity of effects principle: The process is primarily driven by some main effects and low order interactions.
2. The projection property: Fractional factorial designs can be projected into stronger designs in the subset of significant factors.
3. Sequential experimentation: It is possible to combine the runs of two or more fractional factorials to assemble sequentially a larger design to estimate the factor effects and interactions of interest.

Thus fractional factorials are very useful for the screening of factors, and for focusing on the significant main and low order interaction effects. Projecting the significant factors onto a smaller design space creates a stronger design model that can easily be augmented to response surface design (such as central composite designs) for optimisation of the experiment.

A 2^{16-11} resolution IV fractional factorial with 5 centre points was chosen for the screening phase of the experimentation (**Chapter 4**). The resolution of the design refers to the aliasing structure of the design (Montgomery, 2005) such that for a resolution IV design main effects are aliased with 3-factor interactions and two-factor interactions are aliased with other 2-factor interactions. A Centre point is an experiment where each factor is set at its mid value (coded 0), they are added to the design to give an indication of curvature and are replicated (e.g. 5 centre points) to obtain an estimate of the pure error of the design.

3.2.2 Robust Parameter Designs

Robust Parameter Design (RPD) is an approach to product realisation that aims to bring the response as close to the desired target as possible whilst minimising the variability around the target by manipulating control variables and ensuring that the product is insensitive to noise variables (Montgomery, 2005; Rekab & Shaikh, 2005). The philosophy of RPD was developed by Dr. G. Taguchi, whilst Taguchi promoted and used this philosophy with his Crossed-Orthogonal Array design the philosophy has been successfully applied with other factorial and response surface designs.

The original RPD method developed by Taguchi was the crossed array technique[1]. Taguchi separated the control and noise factors into an inner and outer array respectively. The inner array was crossed by the outer array to produce the crossed array design. The results were then analysed using Taguchi's signal-to-noise method. The disadvantages of this approach were that the cross product of the arrays leads to large quantities of experimental runs. Another drawback was the aliasing structure which suffered from confounding of often significant control interaction effects.

Due to the need to model the control-by-control interactions a different approach to the RPD problem was needed. These drawbacks were noted which resulted in the development of combined arrays (Myers et. al., 2009). Instead of separating the control & noise variables they were combined in the same design and the effects analysis saw their separation. A dual response surface approach was then used to analyse the mean model only on the control variables and to analyse the variance model built on the control variables and the noise variable interactions such that the influence of the noise variables could be minimised.

RPD separates influential variables into dispersion effects and location effects. Location effects are variables which only influence the location (*i.e.* mean) of the responses. Dispersion effects are variables which influence the width of the distribution of the responses around the mean (variance) and generally the location of the responses. Other variables are not significant and should be chosen based on the system economics.

According to Montgomery (2005) the focus of RPD is generally:

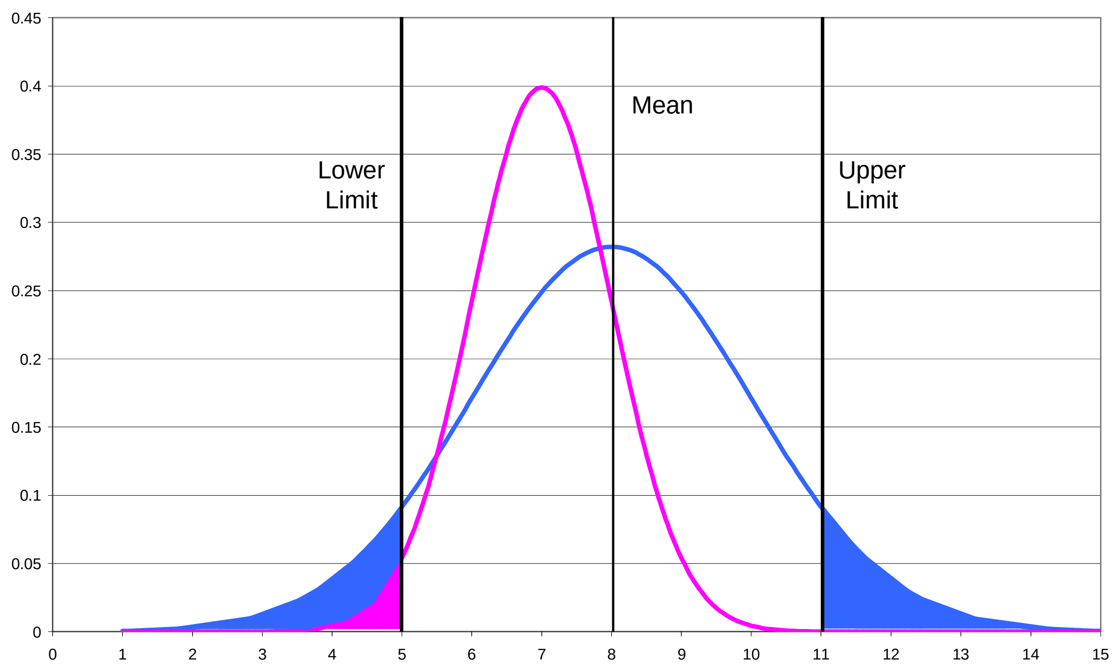
1. Designing a system that is insensitive to environmental factors.
2. Designing a system that is insensitive to variability transmitted within the system.
3. Designing a process that consistently manufactures a product as close to the target specifications as possible in spite of the process input variations.

[1] For more info on this method please refer to *Response Surface Methodology* (Myers et. al., 2009).

4. Determining processing conditions that both bring the output as close to the desired target as possible and minimising the variation around this target output.

Dr G. Taguchi defined quality as a "loss to society" and that the objective of a quality system should be to minimize this loss. This concept is illustrated in Figure 3.2: Illustration of RPD Concept.: the first set of variable settings (blue graph) achieves the desired mean of the process at the expense of increasing the variance around the mean; whilst the second set of variable settings (magenta graph) does not meet the required mean but significantly reduces the dispersion effect. For the specified tolerances the blue graph has significantly more responses outside of specification (Shaded area) as compared to the magenta graph. Therefore although the magenta graph does not have the exact specified mean it has significantly fewer rejected responses.

Figure 3.2: Illustration of RPD Concept.



Along with his philosophy on his approach to quality, Taguchi developed a set of DoE layouts known as crossed arrays (a highly aliased, saturated orthogonal array). These arrays are not ideal due to their aliased structure and therefore it is preferable to use a combined[1] RSM design due to the more favourable design structure (A D-optimal combined array was used for this thesis).

The preferred approach is to use a RSM combined array model without replication. The experimental data will be regressed to a model as described by equation 3.1 with a high degree of power and low correlation between the model terms. The model will be linear with respect to the model parameters

[1] Combined refers to incorporating both the noise and controlled variables in a single design rather than in the case of a crossed array which separates the variables into an inner array of control variables and an outer array of noise variables. The inner array is then replicated for each point of the outer array requiring a significant amount of experimental runs.

(β, γ, and δ) and non-linear with respect to the control (x) and noise (z) variables to allow for non-linear responses and for optimisation. The process can then be optimised using Propagation of Error (PoE).

$$y(x,z) = f(x) + h(x,z) + \varepsilon \tag{3.1}$$

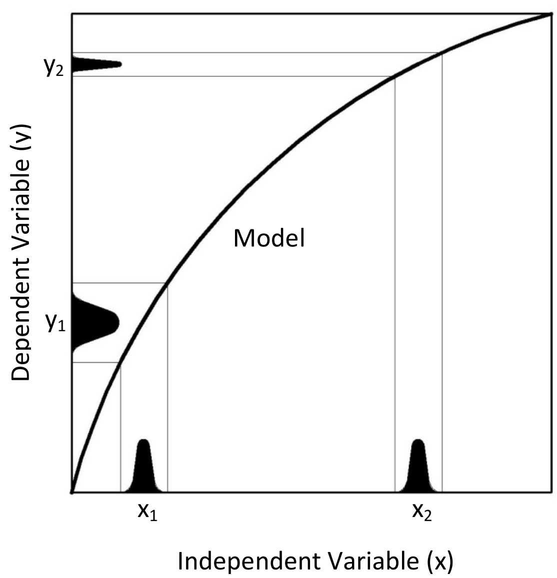
Were,

$$f(x) = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j}\sum \beta_{ij} x_i x_j \tag{3.2}$$

$$h(x,z) = \sum_{i=1}^{k} \gamma_i z_i + \sum_{i<j}\sum \delta_{ij} x_i z_j \tag{3.3}$$

For non-linear responses a method known as Propagation of Error (PoE) can be used to improve the robustness of the modelled system. The method aims to choose the level of the independent variables (factors) which minimise the variation of the dependent variables (responses) for a known variance of the independent variables. Figure 3.3 indicates that for a constant independent variable (x) standard deviation with a modelled non-linear response (y) the level of x has a significant effect of the magnitude of the standard deviation of y.

Figure 3.3: Transmitted Variation



PoE calculates the RPD location and dispersion effects as equations 3.4 & 3.5 respectively (Montgomery, 2005).

$$E_z[y(x,z)] = f(x) \tag{3.4}$$

$$V_z[y(x,z)] = \sum_{i=1}^{r} \left[\frac{\partial y(x,z)}{\partial z_i}\right]^2 \sigma_{z_i}^2 + \sigma^2 \tag{3.5}$$

The POE method was used to minimise the variation of the MVP with the input variation of the polyester.

3.2.3 Design of Experiments: Best Practice

3.2.3.1 Screening Procedure

Carlson & Carlson (2005) recommended the following approach to the screening experimentation of an organic synthesis process:

1. Analyse the synthetic procedure and determine the critical steps. – This step will give a good indication of where to focus the rest of the analysis to obtain the most valuable information.

2. Determine which response to measure. – This can often be the most important step because if you are unsure of the important responses to measure or the measurement method is not accurate enough, no amount of analysis, detailed design or experimentation will provide valuable information.

3. Determine the experimental variables. – This step is important to identify all the variables in the process. A cause and effect diagram is a useful tool to identify all the variables.

4. Categorise the experimental variables as follows: (1) known to have an influence, (2) suspected to have an influence, (3) suspected not to have an influence, and (4) known not to have an influence. – This is where a sound literature survey and theoretical knowledge adds the most value. Use the theoretical knowledge of the system to reduce the required experimentation for the screening DoE.

5. Determine the experimental domain for variables in categories 1 & 2 and if possible category 3. – It is no good taking unrealistic extreme values for the experimental domain as these will produce pointless results. It is also no use to limit the design space to too small a region, as this may exclude optimal or significant regions of operation for the process.

6. Determine if some of the variables can be removed from the experimental list due to constraints imposed by the system. – For example only one grade of a reagent is commercially available therefore testing other grades will be of no value.

7. Define the variables as economically as possible. – There is no commercial value in investigating variable levels that are uneconomical. (There may be academic value in investigating them but this should only be considered if significant).

8. Identify possible interactions (and exclude impossible interactions) – If interactions can be identified early, the DoE can be designed to identify them; in corollary if an interaction can be excluded (e.g. variables that affect different steps in the process) experimentation will not be wasted trying to determine the interaction.

9. Repeat steps 1 to 8. – Do not rush prematurely into experimentation. It is better to re-evaluate the design process and variable selection than to ignore important variables or to include insignificant ones.

10. Suggest a model. – Base this on the expected (estimated) response of the variable, whether linear, non-linear, or interaction responses are expected.

11. Choose an experimental design. – A linear design can be estimated by a simple 2-level factorial experiment, whilst more complex designs will require more complex models. (However it is often most economical to use a 2-level fractional factorial with centre points to estimate non-linearity and use the more complex designs for developing accurate predictive models).

12. Run the experiment, fit the model and evaluate the results. – Run the experiments in accordance with DoE best practice and analyse the results. DoE software (such as Design Expert® 7.0) can simplify the process and aid with the analysis.

13. Interpret the model. – Determine the important variables. Do the results make sense; are they contrary to previous work or the theory? If so were there problems during the experimentation? Should all the experimental results be scrapped or should a few experiments be rerun?

14. Confirm the conclusions. – Use experimentation to validate the results.

15. Proceed to further studies. – Move onto the optimisation stages of the project.

It is important to note that steps 1 to 8 are an iterative exercise which is not solely based on theory. It is important to use ad hoc experimentation, to verify assumptions and to expand the knowledge base as early as possible.

This procedure as recommended by Carlson & Carlson (2005) was followed for the work conducted in Chapter 4.

3.2.3.2 Principals for Experimentation

All the experimental work (**Chapters 4-6**) was run according to DoE best practice as recommended by Anderson & Kraber (1999) and Hybarger (2007):

1. The objectives for the DoE should be determined upfront and not changed during the experimental process.

2. All the responses are measured quantitatively (with the exception of the Build-up which used a non-ideal but acceptable rating scale).

3. Central point replicates should be used to estimate the pure error due to noise in the process.

4. The run order must be randomised to reduce the influence of any uncontrolled time dependent variables.

5. The aliasing structure needs to be understood to ensure that the correct conclusions are drawn.

6. All the equipment and instruments must be calibrated as per the relevant standard or supplier recommendations.

7. The optimal factor level range should be chosen.

8. Factors that are not included in the design must not be varied. This is done to avoid any effects of these "uncontrolled" variables.

It is critical to adhere to these principles to ensure the validity of any conclusions drawn from the results. If these principles are not adhered to, error will creep in and the results become erroneous and should be discarded.

3.2.4 Statistical Analysis

Empirical data tends to be noisy and poorly distributed and therefore requires a robust method of analysis to distil the valuable results and to draw the correct conclusions whilst not violating any of the assumptions required for the statistical analysis.

3.2.4.1 Fitting the Model

Once the experiments have been run and the results compiled, the model can be developed through correct selection of the model terms. Not all the model terms are significant for each response and therefore the statistically insignificant terms need to be removed to prevent over fitting of the data and to develop the most accurate model.

For a fractional factorial design (**Chapter 4**) selection of the significant factors is done by the experimenter using a half-normal plot and Pareto chart. For a RSM design (**Chapter 5**) this is done firstly by selecting a polynomial (e.g. linear, quadratic, cubic) for the basis of the model, choosing the most appropriate model and then applying backward elimination model reduction to remove the insignificant terms to arrive at the best fit model. For all types of designs the model is then analysed by a method known as Analysis of Variance (ANOVA) to determine if the model is significant and that the correct model terms have been selected.

Fractional Factorial Design:

The normal probability plot, which is a graphical technique for determining if an effect is significant or falls within the expected normal experimental variation, was invented by C. Daniel in the 1950s (Lochner & Matar, 1990). It is based upon the Central Limit Theorem which roughly states that as the selected sample size from a population increases the sample will approach a normal distribution (for a strict definition refer to *Design and Analysis of Experiments* by Montgomery (2005) page 31). The half-normal probability plot is a plot of the cumulative normal probability (ordinate) against the factor effect size (abscissa). If the points on the graph fall along a straight line the effects can be said to follow the Central Limit Theory and that the factor effects have no significant influence on the response. If however any factor effects do not fall along a straight line they violate the Central Limit Theorem. These factor effects are greater than would be expected for a normal distribution of responses and can therefore be said to have a significant influence on the response.

The Pareto chart, is a useful plot for visually displaying the effect size of the significant factors on the response, relative to each other. The Pareto chart plots the t-Value of the effect in descending order of magnitude. These t-values are compared to 2 types of calculated t-Limits, the Bonferroni and Standard t-Limits. If the t-value of the effect is larger than the limits then the effect is most likely statistically significant.

Response Surface Model (RSM):

Polynomial selection, firstly the data is regressed to several polynomials and an ANOVA on each model is conducted. The fitted polynomials are then compared against each other for model significance, lack-of-fit, & correlation coefficients.

Model reduction, is applied to the selected polynomial model by backward elimination. Backward elimination, removes the statistically insignificant model terms (in order of magnitude) until only the significant terms remain. The model & terms significance is evaluated by ANOVA after each elimination, until only the significant terms remain.

The Analysis of Variance (ANOVA):

The above models will be subjected to an analysis of variance (ANOVA) to determine if each term is truly significant and if there are any short falls in the expected model.

The Analysis of Variance (ANOVA) is a method used to determine if the effect being tested is significant or not. The logic behind the method is straight forward; the variance between the items (in this case effects) is compared to the variance within the items (between samples) using an F-test. This F-test value is then compared to a critical F-test value to determine if the variance between the effects is significant or if it is comparable to the expected variance due to noise (within the effect.). Illustrated mathematically the sum of squares is represented by equation 3.6 (for main and 2-interaction effects only):

$$SS_{Total} = \sum SS_i + \sum SS_{ij} + SS_E \tag{3.6}$$

The mean sum of squares for each term is then determined by dividing the sum of squares by the number of degrees of freedom. Then a standard test for comparing variances, an F-test, is conducted by comparing the term's variance to the residual variance (equation 3.7).

$$F = \frac{SS_i}{SS_E} \tag{3.7}$$

If the F-value is greater than the F-critical value then the effect can be said to be statistically significant.

The p-value for the test is the probability that the effect with an F-value of its size **did not** have an effect on the response. Therefore, as a general rule an effect with a p-value < 0.05 can be said to have a statistically significant effect on the response at the 95% confidence level.

It is important to note that an ANOVA is only valid under specific assumptions (Garcia-Diaz & Phillips, 1995):

1. Normality of the Residuals – The residual errors are random with a normal distribution around the mean.

2. Sample Independence – The magnitude of the error in one case is not dependent on another.

3. Homoscedasticity (equality of the variances) – The variance is not dependent on the treatment level or location of the response.

These assumptions need to be confirmed to validate the ANOVA results. Unfortunately, this can only be done after the model has been chosen and the responses fitted to the model. The easiest way to investigate the validity of the assumptions is through examination of the residuals.

3.2.4.2 Statistical Validation of the Model Assumptions

After the model has been fitted, the assumptions need to be tested to determine if the model is valid. The diagnostics serve a multitude of purposes:

1. To determine if the assumptions for the ANOVA are satisfied,

2. To identify outlier experimental cases,

3. And to determine if any of the cases has an unduly large influence on the model.

This is done by using various diagnostic plots as listed in Table 3.1. The plots are reviewed and it is up to the experimenter to determine if the plots violate the assumptions or not.[1]

[1] Refer to the work of Kraber et. al. (2005) for a list of examples of what is of concern for each of the diagnostic plots.

Table 3.1: Diagnostic Plots

Plot	Description	Used to Diagnose
Normal Plot of Residuals.	A normal probability plot of residuals for validating the assumption of normality of the residuals.	• Normality of the Residuals.
Residuals vs. Predicted Response.	A plot of the residuals versus the predicted response. Useful for identifying any trends that would violate the assumption of sample independence and homoscedasticity.	• Sample Independence. • Homoscedasticity. • Outliers.
Residuals vs. Run Order.	A Plot of the Externally Studentized[1] residuals versus the run order for identifying trends. Outliers are easily identified if they fall outside the t-limit (red line). A trend in the run order would indicate the dependence of the samples on the time progression of the experiment (This should have been included as a blocking or co-varying factor).	• Sample Independence. • Homoscedasticity. • Outliers.
Cook's Distance.	A measure of how much the regression changes if the sample is deleted. This indicates how much influence a sample has on the overall model. If the leverage is too large, this can indicate that the model is inadequate or the sample is an outlier.	• Leverage. • Outliers.
Predicted vs. Actual Response Plot.[2]	This gives a quick indication of regions where there are significant model inadequacies and which regions of the design space will be difficult to predict. Ideally the plotted points should lie along a 45° line.	• Outliers. • Model inadequacies.

[1] The residuals are Externally Studentized (aka: Outlier t-value) by estimating the response from the model regressed from all the responses with the exception of the response in question. This tests whether the run in question is consistent with the other data. (Stat-Ease, 2005).

[2] Primarily useful for the final predictive model and not the one for the screening experiment. However it is included for interest's sake and can give a qualitative indication of regions in the design space which may become a problem.

3.3 Dimensional Analysis Empirical Model

> "Dimensional analysis is based upon the recognition that a mathematical formulation of a chemical or physical technological problem can be of general validity only if it is *dimensionally homogenous"*
>
> \- Marko Zlokarnik (2006)

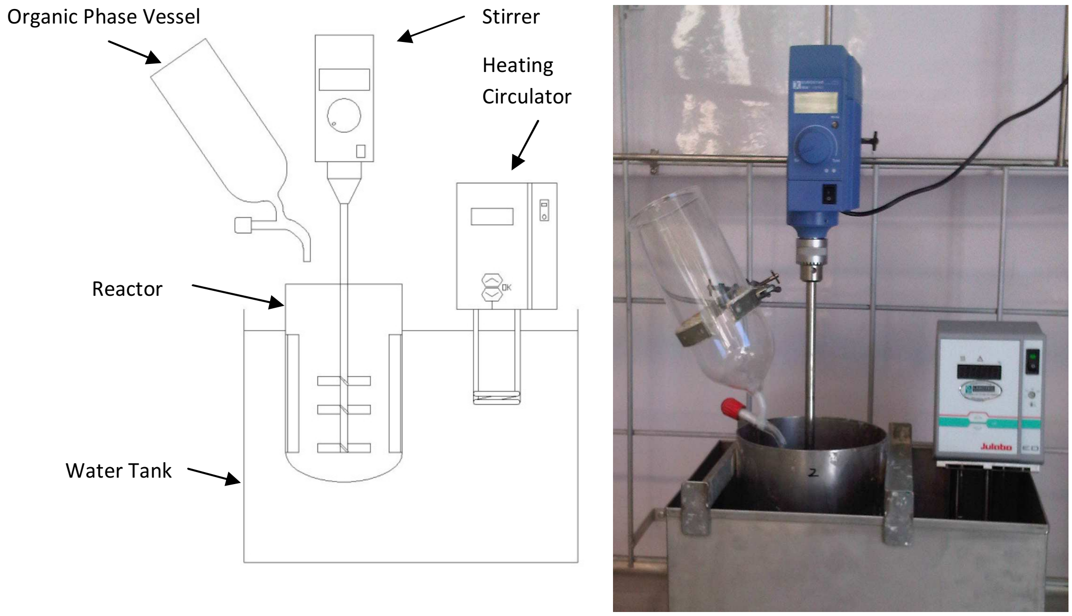
Dimensional analysis models experimental data based upon dimensionally homogenous data sets of physical properties and characteristics of a system. The most common form for the modelling of experimental data using dimensional analysis is to create dimensionless groups and determine the mathematical relationship between the dependent dimensionless group as a function of the independent dimensionless groups.

The Buckingham-Π method is a method for taking a dimensionally homogenous system of (n) parameters and reducing it to a smaller set of (n-m) dimensionless groups for analysis, where (m) is the number of dimensions (e.g. length or mass). These dimensionless (semi-)empirical models in conjunction with the principles of similitude are readily useable for the scaling-up or scaling-down of processes.

A dimensional analysis of the characteristics of the MVP batches from the RPD design was conducted to develop an empirical dimensionless model (DM) for the MVP.

3.4 MVP Manufacturing Process

Figure 3.4: MVP Lab Reactor Setup.



The initial formulation, raw materials and process were outlined in Chapter 2.3. Each experiment was recorded in a standard form (Appendix A) which reflected the differences for each experimental run. The following is a detailed description of each step in the experimental process:

Stage 1: Aqueous Phase Preparation

1. Prepare the aqueous phase by thoroughly mixing until homogenous, the PVOH, HEC and Initial Water at their specified quantities in a bucket.

2. Place the reactor into the water bath and using ice and the heating circulator set the bath temperature to the specified temperature.

3. Pour the aqueous phase into the reactor and adjust the stirrer blade to the correct height. Allow the aqueous phase to reach the correct temperature under low speed mixing to aid heat transfer.

Stage 2: Organic Pre-Dispersion

4. Once the aqueous phase has reached the specified temperature, charge the UPR and titanium dioxide pigment into a bucket and disperse at high speed with the high shear Saw-tooth mixer for 10 minutes.

5. Reduce the speed and slowly add the styrene to the dispersion. Allow to mix for 2 minutes.

6. Slowly add the LMA and mix for 2 minutes.

7. Simultaneously add the DETA to both the aqueous and organic phases in their respective quantities and mix for 5 minutes. A temperature rise should be noted in the organic phase.

Stage 3: Addition and Emulsification

8. Decant the organic phase into the glass pouring vessel. Set the stirrer speed to the desired rpm.

9. Slowly add the organic phase to the aqueous phase at a constant rate over the specified time period

10. Allow the suspension to mix for the specified emulsification time.

Stage 4: Initiation

11. Dissolve the Ferrous Sulphate in water and add slowly to the reactor. Allow to mix for 3 minutes.

12. The Cumene Hydroperoxide is then added to the reactor and mixed for 3 minutes.

13. The stirrer is then stopped for a pre-specified period of time.

Stage 5: Curing

14. After the stirrer stationary period the stirrer is restarted at a low speed.

15. The water bath temperature is set to 50°C and the temperature increase is controlled over a period of 30 minutes.

16. The temperature is held at 50°C for one hour. The stirrer speed is increased to counter act the increase in viscosity that occurs during curing.

Stage 6: Temperature Ramping

17. The temperature is then ramped to 60°C over 30minutes.

18. Once the temperature reaches 60°C it is held at 60°C for 3hours to reduce the free monomer in the product.

19. The water bath is then turned off and the Reactor is allowed to cool overnight.

Stage 7: Post Treatment

20. The next morning the reactor contents are scraped out and the MVP suspension is decanted into a bucket.

21. The MVP suspension is then mixed under the saw-tooth high shear disperser.

22. Slowly add the surfactant to the MVP and allow to mix for 10 minutes.

23. Slowly add a pre-mixed aqueous solution of ammonia and mix for 10 minutes.

24. Slowly add the premixed HASE thickener and water to the MVP and mix for 10 minutes.

25. Add the acticide to the mixture and stir for 5 minutes.

26. Remove for the high shear saw-tooth disperser and conduct all necessary testing on the sample.

3.5 Analytical Methods

3.5.1 Specific Gravity (Density)

The specific gravity is a measure of the density of the fluid relative to a reference fluid (in this case water at 1.000 $kg.dm^{-3}$) it is easily converted to the units $kg.m^{-3}$ but is most often reported in its dimensionless form. A low SG is desirable since paint is generally manufactured and cost determined on a per kg basis and sold on a per volume basis therefore the lower the SG the more paint can be sold at a lower cost.

The specific gravity is measured using a 100cc Sheen Pyknometer Cup (mass per volume cup) following the Plascon Test Method PTM 0038 (2009). The basic principle of the test method is the weight of the empty and filled cup is determined and the difference is the mass of the volume of fluid in the cup. The cup maintains a constant volume of fluid as any excess fluid flows out of a small hole at the top of the cup and is then removed. Therefore the mass of the 100cc of fluid is calculated and the specific gravity is determined from the mass.

3.5.2 pH

The MVP immediately after production has a pH of approximately 6. The HASE thickener used to stabilise the suspension and prevent settling requires a pH above 7.0 (preferably 7.0-8.5) to thicken the dispersion (Rohm & Haas, 2001). Therefore it is important to measure the pH to ensure that it is within the required range.

The pH is measured using a Metrohm 744 pH meter and a Methrohm Porolyte glass pH electrode according to the manufacturer's specifications. The pH probe was calibrated and used in accordance with the manufacturer's instructions (Metrohm, *Sinne Anno)*

3.5.3 %NVC

The %NVC is the non-volatile component of the suspension expressed as a percentage. It is an indication of the solid component by mass of the suspension. This is important since it gives an indication of the contribution of the mass solids to the final coating when used in paint. It however does not give an indication of the final volume solid contribution to the paint since the particle density fluctuates depending on the degree of vesiculation of the particle.

The Non-Volatile Content (%NVC) or Total Solids Content (%TSC) measures the quantity by mass of the suspension that is not volatile below 120°C. The method is as follows:

> A foil tray is weighed and the mass recorded. A sample of the MVP dispersion (~1.0g) is spread thinly on the foil tray and then the mass is recorded. The sample is then placed in an oven at 120°C overnight to ensure that all the volatiles have evaporated. The tray is removed from the oven, allowed to cool and reweighed. The %NVC is calculated by mass balance (equation 3.8).

$$\%NVC = \frac{(Mass\ after\ heating - Mass\ foil\ tray)}{(Mass\ before\ heating - Mass\ foil\ tray)} \tag{3.8}$$

3.5.4 Viscosity

The Brookfield viscosity is a single point apparent viscosity measurement used as an indication of the flow characteristics and stability of the dispersion. However the dispersion has viscoelastic properties and therefore a full rheological profile would be needed to represent the flow behaviour of the dispersion.

The rheology of the dispersion is an important parameter of the MVP as it gives an indication of the flow characteristics of the dispersion as well as a qualitative indication if the dispersion will settle during storage or if there is the likely hood that the formulation may form a gel in the reactor during scale-up.

The apparent point viscosity of the MVP dispersion is measured using a Brookfield Viscometer Model DV-1+. The viscometer uses a range of spindles at various speeds to measure the apparent viscosity of a fluid by applying a constant shear rate and measuring the shear stress applied by the fluid. The apparent viscosity is temperature dependent and therefore the sample is only measured once it is stable at 23±2°C. The apparent viscosity is measured in cP at 30rpm using a #63 or #64 spindle.

Whilst the author acknowledges the MVP exhibits a pseudo-plastic (as well as thixotropic) rheological behaviour (Moolman, 2003) it is beyond the scope of this thesis to investigate the rheology of the MVP dispersion.

3.5.5 Reactor Holdup Ratio

The reactor holdup ratio is the volume fraction of the reaction mixture that is in the dispersed phase and can be calculated as follows:

$$\phi = \frac{\rho_d M_d}{\rho_d M_d + \rho_c M_c} \tag{3.9}$$

3.5.6 Contrast ratio

Opacity is the ability of a substance to optically obliterate its substrate. One such measure of opacity is known as the contrast ratio which is the ratio of reflectance of a film (usually paint) over a standardised black substrate to its reflectance (of the same film thickness) over a standardised white substrate. The higher the contrast ratio the less the substrate influences the reflectance readings (white has a very high reflectance whilst black has a very low reflectance) and therefore the higher the ability of the substance to obliterate the substrate.

Whilst opacity is a critical property of paint it is not so for the Suede MVP, however it gives an interesting qualitative understanding of whether vesiculation has occurred (vesicles improve opacity due to their ability to scatter light) and the particle size distribution (a wider distribution packs better as a film and therefore increases opacity).

The method used follows ASTM D2805-96a (2003): A film is applied to a black and white Leneta chart with a 200micron film applicator. The wet film thickness is measured to ensure that the film is of sufficient thickness for the test (Opacity and hence contrast ratio is dependent on the thickness of the substance). The film is then allowed to dry overnight. Using the MacBeth ColorEye®, the reflectance over the black and white portion of the Leneta chart is measured and the contrast ratio is determined from the measurements.

3.5.7 Buildup

Buildup is an estimated observation made on the degree of gel buildup at the edge of the reactor. It is evaluated visually on an interval scale of 0 (no build-up) to 5 (buildup covers entire reactor). A buildup of less than 2 is preferred with 3 only being accepted if the reactor has rotating baffles acting as scraper blades.

The buildup in the reactor occurs due to the increasing thixotropic effect of the suspension. Due to the low shear rate at the edge of the reactor the suspension's apparent viscosity increases until the shear rate applied can no longer cause the fluid to flow. This effect can be so severe that the fluid will only flow in the immediate vicinity of the stirrer due to the shear in this region. This is why the surfactant is added post treatment to reduce this shear thinning behaviour of the MVP.

Buildup refers to the gel that forms along the edge of the reactor during the heating phase of the process; if this is excessive the reactor contents can gel (in extreme cases inversion is known to happen) which will require manual removal of the product from the reactor. Whilst build-up is highly correlated with the rheology of the product (before post treatment) there is currently no quantitative measure for it. Therefore a qualitative determination using a 1-5 scale is made by the experimenter according to the pictures in Figure 3.5. Whilst a low (0-1) buildup poses no processing problems and medium buildup (2) requires external circulation of the reactor contents and an increased stirrer speed during the heating phase to prevent the reactor from needing to be manually cleaned. A high buildup rating (3-5) formulation should not be scaled-up due to the processing problems that will occur.

Figure 3.5: Qualitative Buildup Ratings

Buildup = 0

Buildup = 1

Buildup = 2

Buildup = 3

Buildup = 4

Buildup = 5

3.5.8 Particle Size Distribution (PSD)

The particle size distribution is one of the defining characteristics of the MVP. The suede effect of the MVP is almost exclusively determined by its PSD. Therefore it is critical to determine accurately and will be used as one of the optimisation criteria for this thesis.

The particle size distribution (PSD) throughout this thesis was measured using a HELOS/BF® Laser Diffraction sensor coupled with an offline SUCELL® suspension cell manufactured by Simpatec GmbH. The method applied was Low Angle Laser Light Scattering (LALLS) and relies on the principle that diffraction angle is inversely proportional to the particle size (Rawle, *sinne anno*). The instrument measures a PSD from 0.5 to 175µm.

Figure 3.6: HELOS & SUCELL Optical LALLS Setup

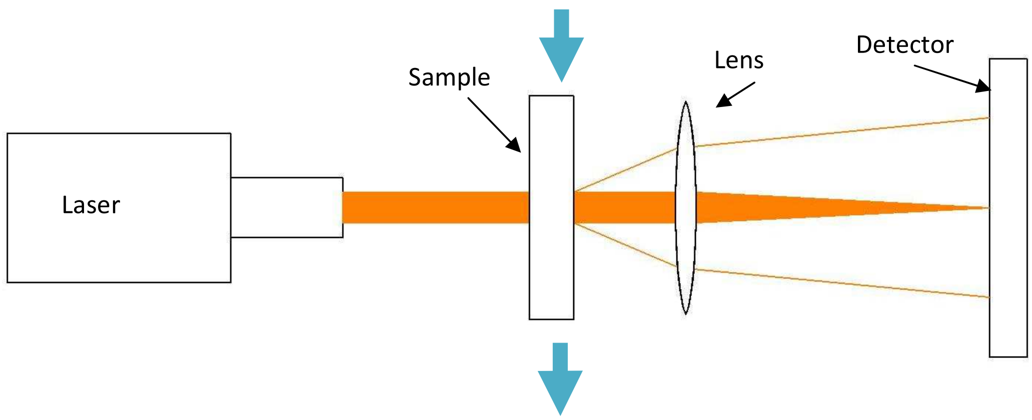
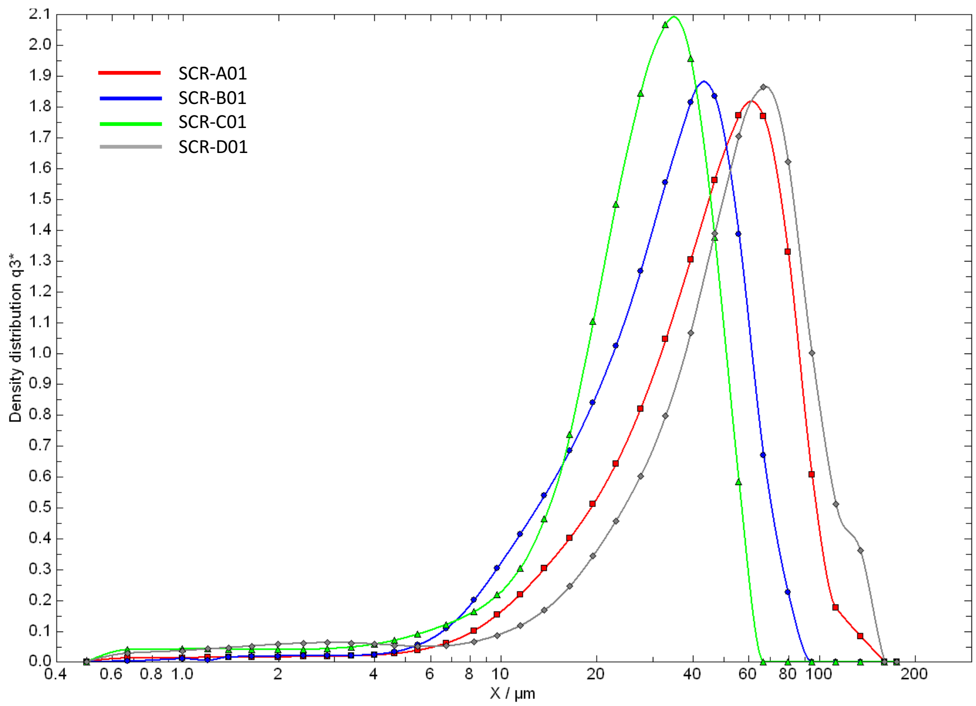


Figure 3.6 illustrates the basic optical LALLS setup referred to as Fourier Optics (Puckhaber & Röthele, 1999). A laser of fixed wavelength (He-Ne gas laser; λ = 0.63µm) is expanded and passed through the sample. (In this case the sample is a dilute suspension of particles turbulently passed through a suspension cell). The scattered light is focused by passing it through a lens system. The focused light is then detected by a suitable detector (usually a photosensitive silicon slice with a number of detectors (optimum 16-32 detectors)) (Rawle, *sinne anno*). The diffraction patterns are then analysed by the software and a particle size distribution is determined.

The software uses Fraunhofer diffraction physics originally developed in 1820 ('Kap 3 …', 2006) to calculate the PSD which has the distinct advantage over other theory (e.g. Mie theory) since it requires no parameter inputs. Mie theory requires that the refractive index and absorption coefficient of the particles and suspending fluid are known. The nature of the MVP is that the number and size of the vesicles in the particles differ randomly for every particle and have been observed to have a dependence on the particle size (larger particles have been observed to have more vesiculation). Therefore due to the random nature of the vesicles and difference in refractive index between the vesicle and the particle the overall refractive index for every particle will be random and unique. Due to the then unknown refractive index of every particle the more accurate Mie theory cannot be used to calculated the particle size distribution. However the Fraunhofer diffraction theory does not suffer from this dependence on known parameters and is therefore well suited for determining the PSD of the MVP.

Figure 3.7: VMD Particle Size Distribution.



The PSD can be represented in a single value as the mean. The mean for a specific size distribution will depend not only on the definition of the characteristic length[1] but also on the calculation method used. The simplest calculable mean is the number-length-mean diameter (d_{10}) which is simply the summation of the diameters divided by the number of particles ($\sum d/n$). This mean tends to favor large quantities of small particles over a few large particles.

However if the volume of the particle is of interest the d_{10} diameter can be misleading and a number-volume-mean diameter (d_{30}) can be calculated, $\left(\sqrt[3]{\sum d^3/n}\right)$ which is weighted towards particles of a larger volume. The disadvantage of these methods is the number of particles is inherent in the formulae requiring a large number of particles to be explicitly counted (Rawle, *sinne anno*).

To overcome this problem of counting the particles a moment-mean can be used; the two most common being the Sauter-Mean-Diameter (Surface Area Moment Mean), (d_{32}) and the De Brouckere-Mean-Diameter (Volume Moment Mean) (d_{43}). The generic equation for calculating the mean is:

$$d_{ij} = \left(\frac{\sum d^i}{\sum d^j}\right)^{1/i-j} \tag{3.7}$$

[1] Whether it is the diameter of a sphere of the minimum length, maximum length, same volume, surface area, etc.

Thus giving the Sauter-Mean-Diameter (SMD) as:

$$d_{32} = \left(\frac{\sum d^3}{\sum d^2}\right)^{1/3-2} = \frac{\sum d^3}{\sum d^2} \tag{3.8}$$

And the De Brouckere-Mean-Diameter (VMD) as:

$$d_{43} = \left(\frac{\sum d^4}{\sum d^3}\right)^{1/4-3} = \frac{\sum d^4}{\sum d^3} \tag{3.9}$$

The above mean diameters will be used to characterise the particle size distribution of the MVP (with particular focus on the VMD). It is particularly important to note a DoE response for a multiple regression model needs to be a single value as the DoE method used cannot handle data as a function. However to include the spread of the particle distribution, both the standard deviation of the PSD and the coefficient of variance will be examined.

The width of the PSD is important to characterise, since a narrow distribution of particle sizes will provide a vastly different suede effect to a wide PSD. This is generally characterised as the standard deviation (SDev):

$$\sigma = \sqrt[2]{\left[\int_{-\infty}^{\infty} (x-\mu)^2 f(x) dx\right]} \tag{3.10}$$

The SDev has the same units as the measured variable (In this case, microns).

The SDev is dependent on the location of the mean of the sample distribution and therefore should not be compared for samples with significantly differing means. To compare the relative width of a distribution independent of the location of the mean, the coefficient of variance is used. The coefficient of variance is defined as the SDev divided by the mean and is represented as a percentage; it is independent of the location of the mean and therefore can easily be compared for PSD with considerably different means.

$$\%CV = {}^{SDev}/_{Mean} = {}^{\sigma}/_{\mu} \tag{3.11}$$

3.5.9 Rheology Flow Curve

As with many polymers the MVP and the separate organic & aqueous phase display non-Newtonian rheological behaviour. Whilst a full rheology analysis is beyond the scope of this thesis[1] the measurement of the rheology of the organic & aqueous phase is critical for conducting a dimensional analysis of the system and hence for developing an empirical dimensionless model.

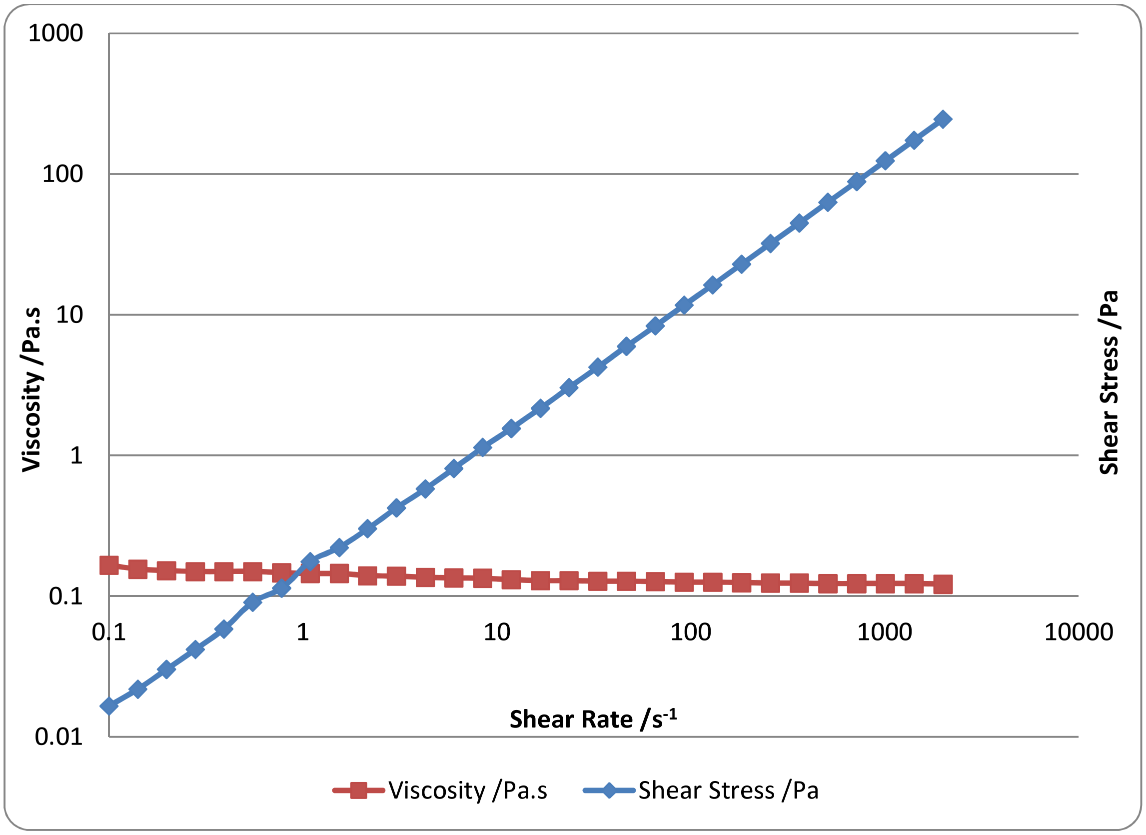
Only the rheology flow curves (Figure 3.8) of the two phases were measured. This provides information on how the shear stress of the fluid varies with shear rate and can then be used to calculate the viscosity profile of the fluid.

The flow curves were measured on a Paar Physica® Modular Compact Rheometer (MCR 300) using the cone and plate (CP) method. The fluids' flow curves were measured under a controlled shear rate

[1] Refer to *Rheology of Coatings Systems,* by Moolman (2003) for the rheology of the MVP.

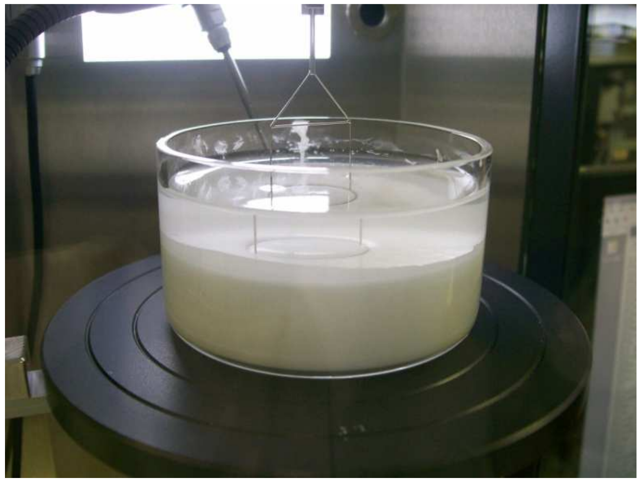
mode by measuring the generated torque and then calculating the shear stress. The CP was used as it is designed for high shear rates of up to 7000s^{-1} and has the advantage over other methods in that it has homogenous shear conditions across the diameter of the CP. The flow curves were then used to calculate the apparent viscosity for a given shear rate as determined by the mixer speed in the reactor.

Figure 3.8: Rheology Flow Curve: SCR-C01 Organic Phase.



3.5.10 Interfacial Tension

Figure 3.9: Interfacial Tension Measurement



The interfacial tension (IFT) between the organic and aqueous phases is critical in determining the particle size and is frequently observed in empirical equations found in literature as part of the Weber number. This critical property will be used as part of the empirical dimensionless model developed in **Chapter 6**.

The IFT was measured using a Krüss K11 MK3 Tensiometer. The method used was the push ring method with a Platinum-Iridium Du Noüy ring (wetted length 119.99mm) and the Huh & Mason correction method (Based upon the ASTM method D971-99a (2004)). The Du Noüy ring (Figure 3.9) is frequently cited in literature (Vivaldo-Lima, 1997; Jahanzad, 2005; Hashim & Brooks, 2004; Chatzi et. al., 1989) as the method used for measuring the IFT for suspension polymerisation model development. In this case the push method is used as the higher surface tension liquid (aqueous phase) is the lower density phase and therefore the ring needs to be pushed from the aqueous phase to the organic phase.

$$\sigma = C\frac{F_{max}}{L_W \cdot \cos\vartheta} \qquad (3.12)$$

The interfacial tension is equal to the maximum force (F_{max}) applied divided by the wetted length. For a Du Noüy ring, the maximum force is reached when the contact angle (θ) is zero. The correction factor (C) is needed to subtract the weight of the fluid from the maximum force as well as to compensate for the different wetted lengths on the inside and outside of the ring. In this case the Huh & Mason correction was used.

3.6 Nomenclature

Latin Variable	Description	Units
%CV	Coefficient of Variance	Percentage
C	Correction factor	-
d	Diameter	M
E[]	Mean function	-
f()	Function	-
F	Force	mN
h()	Function	-
L	Length	M
M	Mass	Kg
n	Number of Particles	-
SS	Sum of squares	-
V[]	Variance function	-
x	Factor value	-
y	Response variable	-
z	Noise factor	-
Greek Variables	**Description**	**Units**
β	Control factor regression coefficient	-
γ	Noise factor regression coefficient	-
δ	Control × noise factor regression coefficient	-
ε	Error	Unspecified
θ	Contact Angle	Radians
μ	Mean	-
ρ	Density	$kg.m^{-3}$
σ	Interfacial tension	$mN.m^{-1}$
	Standard deviation	Unspecified
ϕ	Hold-up ratio	-

Subscript	Description	Subscript	Description
0	Mean	10	Number length mean
32	Sauter-mean	43	De Brouckere-Mean
c	Continuous	d	Dispersed
i, j,	Generic reference	max	Maximum
W	Wetted		

4 Screening Experimental Phase

4.1 Introduction

Screening (DoE) -

'Sifting through a large number of factors with the fewest number of experiments.'

It is almost impossible to theoretically predict all the variables which will have a significant effect on a particular chemical process or system. Therefore it is important to experimentally determine which variables significantly affect the system as well as the ranges for which the variables have this significant influence. It is neither advantageous nor economical to optimise all the variables in the hope of obtaining the optimum solution as this becomes both costly and time consuming. Neither is there any advantage to using a shotgun experimental strategy as this will at best find a sub-optimal solution or at worst be a complete waste of time and resources, resulting in a failed project, process or product.

Screening is used to evaluate all the possible factors and to select only the significant ones for further experimentation such as modelling and optimisation. Screening is used to obtain information about which factors are important, and the range for which they are significant for the minimum cost (i.e. minimum number of experiments).

Whilst in general experimentation is unavoidable for developing and optimising a chemical product, this does not mean that all systems should be approached as a black box; theoretical knowledge still can add incredible value to the development, modelling and optimisation of the system. Therefore it is important when approaching a new chemical process or especially when optimising a poorly understood process that all the theoretical and practical knowledge of the system be taken into consideration. This can require some creativity on the behalf of the experimenter and many assumptions will be required to reduce the possibly infinite number of variables to a more manageable select few.

Therefore the employment of the right screening procedure is critical to reduce the cost & duration of a project as well as to obtain the best understanding of the process system as a whole.

4.2 Objectives

The objectives of this section are to:

- Define the key characteristics of the Suede MVP.
- Determine all of the system's factors.
- Screen all the factors to determine the significant one.

The desired outcome is to obtain an understanding of the raw materials & process and how each variable affects the final product. A better understanding of the variable tolerances of the process will indicate where increased control over the system will be required.

4.3 Design of Experiments: The Design

The system was originally analysed in the work by Terblanche (2002) and Engelbrecht et. al. (2006). The critical steps have been discussed in chapter 2.3.3 (Formulation) and chapter 2.3.4 (Manufacturing Process) and chapter 3.4 (Manufacturing Process).

4.3.1 Determining the Measured Responses

It is critical to determine the relevant measured responses as this dictates all future experimentation and the focus of the project. Typically for suspension polymerisation the Sauter-Mean Diameter (d_{32} or SMD) has commonly been used to characterise the particle size distribution. However previous work by the author (Clarke, 2009a) found that the Volume-Mean Diameter (d_{43} or VMD) gave a better indication of how the Particle Size Distribution (PSD) of the MVP influenced the Suede effect of the Suede paint (the primary usage of the Suede MVP particles). This conclusion was validated by these experiments due to the higher correlation between the coarseness of the paint's suede effect to the VMD (0.92) compared to the SMD (0.71).

Other responses of interest are the rheological properties of the MVP dispersion. A detailed rheological analysis of the MVP is beyond the scope of this thesis, however the rheology was indirectly investigated through the buildup in the reactor (a qualitative indication to whether the reactor contents will gel), and the Brookfield apparent viscosity.

However, to avoid losing valuable information at this stage of the experimentation it was determined that as many responses as was economically possible should be measured to avoid losing critical information. Therefore all the responses listed in Table 4.1 were investigated.

Table 4.1: List of Response variables measured in the Screening Phase[1]

Particle Size Distribution	General Properties	Influence on Paint
Sauter-Mean Diameter (SMD)	Build-up (Qualitative)	Coarseness (Qualitative)[2]
Volume-Mean Diameter (VMD)	Specific Gravity	Tint Strength[3]
Standard Deviation of SMD (SDevS)	Non-Volatile Content	
Standard Deviation of VMD (SDevV)	Brookfield Viscosity	
Coefficient of Variance (SMD)	Contrast Ratio	
Coefficient of Variance (VMD)		

[1] Only the Volume-Mean Diameter and Build-up analysis will be detailed here, the other measured responses analysis results appear in Appendix C3.

Note: The tables and specific information for the variables are based on the final iteration of the screening process conducted.

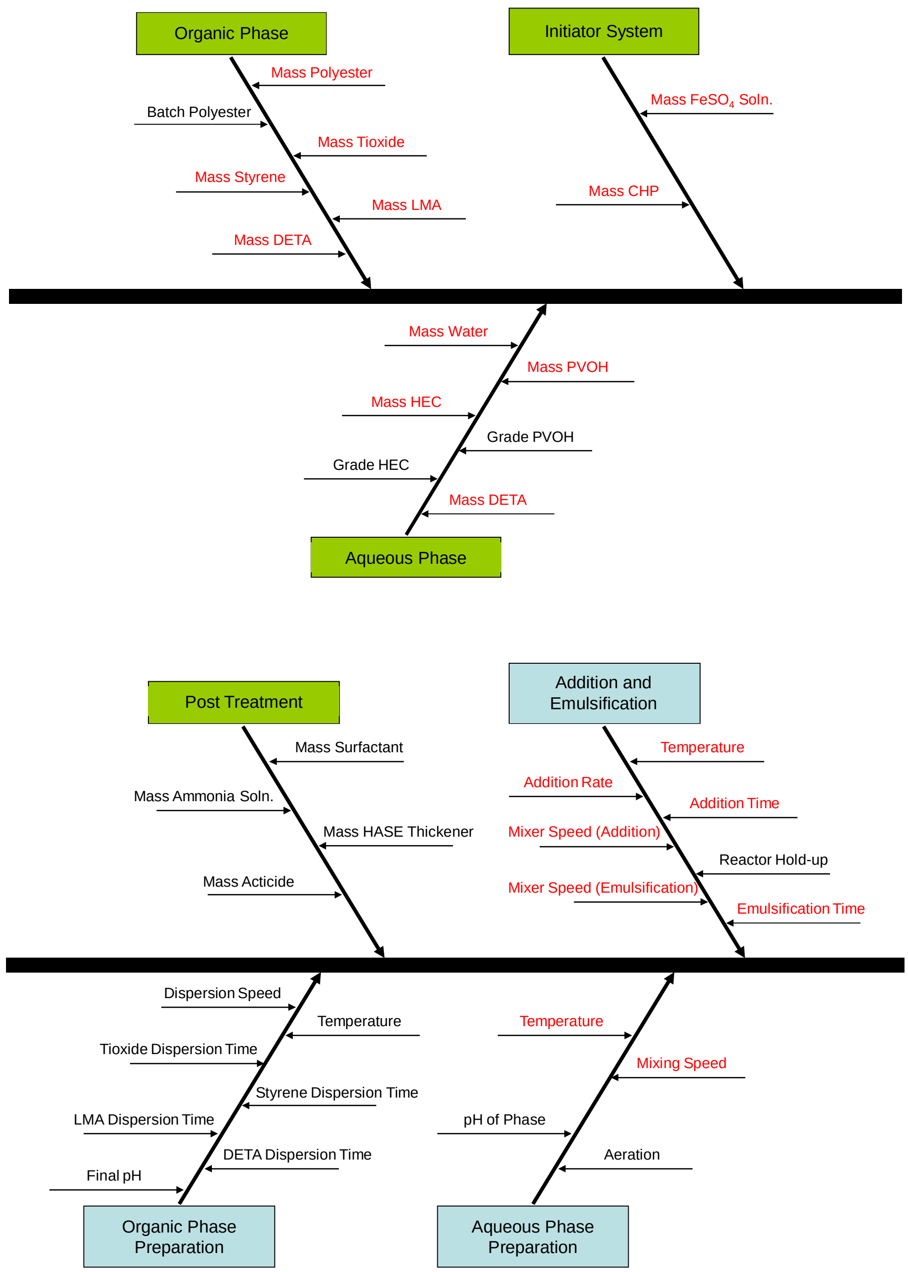
[2] Qualitative Visual rating (0-5) 0 being very fine and 5 being very coarse.

[3] *CRGI Test Method 73* (*sinne anno).*

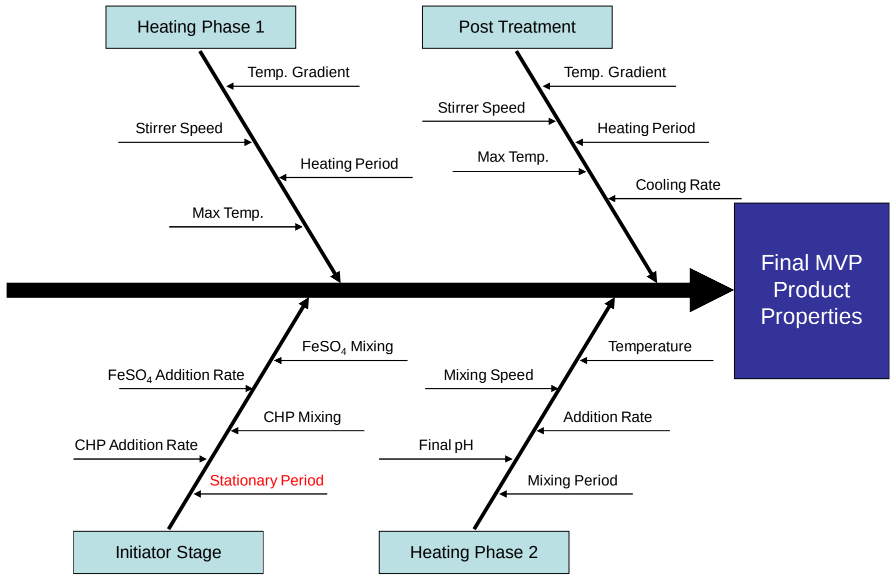
4.3.2 Determining the Experimental Factors.

An initial analysis of the system identified a possible 55 factors (Figure 4.1) which could possibly have a significant effect on the system.

Figure 4.1: Ishikawa (Cause and Effect Diagram)[1]



[1] The short list of 16 variables tested in the screening experimentation are in red.



To test all 55 identified variables would require an unrealistically large number of experimental runs. Therefore the list was reduced to a manageable number of factors for the experimentation. The identified variables were categorised into 4 groups ([1] known to have an influence, [2] suspected to have an influence, [3] suspected not to have an influence, and [4] known not to have an influence) using information obtained from several simple ad hoc experiments, theoretical knowledge of the system as well as practical experience with the system by the author and other persons familiar with the system. The list was reduced to 16 factorss (Table 4.2) that needed to be tested experimentally.

For example all variables that affect the MVP after the particle identification point[1] were determined to have a negligible impact on the PSD (Category 4). The particle identification point was determined experimentally (Appendix C.2) to occur 30minutes after catalysis.

A full list of the identified variables as well as their final allocated category values and justification for the classification is available in Appendix C.1.

[1] The particle identification point is described by Jahanzad et al. (2005) as the point when the liquid-liquid dispersion behaves like a solid-liquid dispersion. The dispersed drops viscosity increases to the point where they behave like solid particles, they no longer break-up or coalesce and a constant particle size and distribution is achieved.

Table 4.2: Factor List for Screening Experimentation.

No.	Factor	Category	- Level	0 Level	+ Level
1	Mass UPR	2	-10%	0%	+10%
2	Mass TiO_2	3	-25%	0%	+25%
3	Mass Styrene	2	-15%	0%	+15%
4	Mass LMA	2	-20%	0%	+20%
5	Mass DETA (Organic Phase)	2	-20%	0%	+20%
6	Mass Water	2	-6%	0%	+6%
7	Mass PVOH Soln.	2	-10%	0%	+10%
8	Mass HEC Soln.	2	-10%	0%	+10%
9	Mass DETA (Aqueous Phase)	3	-20%	0%	+20%
10	Mass Ferrous Sulphate	3	-20%	0%	+20%
11	Mass CHP	3	-20%	0%	+20%
12	Initial Reactor Temperature	2	15°C	22.5°C	30°C
13	Stirrer Speed[1]	1	270rpm	300rpm	330rpm
14	Addition Rate	2	5min	10min	15min
15	Emulsification Time	2	10min	20min	30min
16	Stationary Period	2	0min	20min	40min

The justification for each factor level choice for the Screening Experimental Phase is as follows:

1. **Mass UPR:** ±10% of the mass of the UPR has a ±1.5% effect on the theoretical non-volatile content of the final product. This is within an acceptable range for the product as too high a theoretical %NVC risks suspension inversion or product gelling and too low a %NVC leads to an uneconomical product.
2. **Mass TiO_2:** TiO_2 is less than 1% of the formulation. A ±25% variation would be acceptable especially if the TiO_2 level can be reduced as low as possible.
3. **Mass Styrene:** A ±15% variation in styrene has a ±1% effect on the theoretical %NVC which is within acceptable limits.
4. **Mass LMA:** Due to the small quantity of LMA used (0.68%) a ±20% deviation will have a minimal influence on the %NVC. It has been observed that a deviation in amount of this raw material has a significant effect on the PSD (Engelbrecht et. al., 2006).
5. **Mass DETA in the Organic Phase:** (0.21%) of formulation. DETA is known to have a significant effect on the final product. A ±20% deviation was necessary to compensate for the error associated with the expected errors during measurements due to the small quantities measured.

[1] Based on the 5L scale reactor.

6. **Mass Water:** A ±6% deviation on the mass of water has a ±3% deviation on the %NVC. The water deviation needs to be limited to prevent the %NVC from becoming either too high or too Low.
7. **Mass PVOH Soln:** ±10% deviation for the PVOH would give an indication whether the level of PVOH has an influence on the PSD without creating extreme values of %NVC.
8. **Mass HEC Soln:** ±10% deviation for the HEC would give an indication whether the level of HEC has an influence on the PSD without creating extreme values of %NVC.
9. **Mass DETA in the Aqueous Phase:** (0.06%) of formulation. A ±20% deviation was necessary to compensate for the error associated with the expected errors during measurements due to small quantities measured.
10. **Mass Ferrous Sulphate:** (0.01%) of formulation. A ±20% deviation was necessary to compensate for the error associated with the expected errors during measurements due to small quantities measured.
11. **Mass Cumene Hydroperoxide (CHP):** (0.12%) of formulation. A ±20% deviation was necessary to compensate for the error associated with the expected errors during measurements due to small quantities measured.
12. **Initial Reactor Temperature:** The plant is based in Durban and therefore the temperature of the aqueous phase may reach a temperature of as high as 30°C and is not expected to reach temperatures below 15°C. (Chilled water is available).
13. **Stirrer Speed:** On the 5L scale a ±25rpm has been observed to have an effect on the PSD of the MVP therefore the variation in speed was set to ±10% (±30rpm) of the standard speed.
14. **Addition Rate:** A ±50% deviation of the addition period should indicate if the addition rate has a significant influence on the PSD.
15. **Emulsification Time:** A ±50% deviation of the emulsification period should indicate if the emulsification period has a significant influence on the PSD.
16. **Stationary Period:** The stationary period was believed to be required to allow time for the initiator to migrate to the organic phase. Theron (2000) and Engelbrecht (2002) reported that this may not be the case for the MVP system; therefore the low level of the stationary period was set to zero and the high level double the standard value of 20minutes.

4.3.3 Determining the Design Layout.

The nature of the responses (VMD, Build-up and other responses) are currently unknown. Since this experimental phase is purely for screening of the variables the number of experiments required for complex models (polynomial and other non-linear models) make them undesirable. Generally a linear model is chosen for screening experiments due to their simplicity and economy. Centre points can be added to the model to obtain an indication of any non-linearity's in the system that the current chosen model does not cater for.

For the screening phase of this thesis a linear model (equation 4.1) will be regressed from the 32 design points and 5 centre points using the Design Expert 7® (DX7®) software.

$$y = \beta_0 + \sum_{i=1} \beta_i x_i + \varepsilon \tag{4.1}$$

The design chosen for the screening phase of the experimentation was determined with the aid of Design Expert 7® and is as follows:

Type:	2-Level fractional factorial.
Factors:	16 factors.
Resolution:	IV
Generators:	F=ABC; G=ABD; H=ACD; J=BCD; K=ABE; L=ACE; M=BCE; N=ADE; O=BDE; P=CDE; Q=ABCDE.
Design Points:	32.
Centre Points:	5.

Two-Level fractional factorials (2FF) are commonly used for screening experiments (Montgomery, 2005) due to their simplicity and economy (minimal cost for most information). They however suffer from aliasing of the factor effects. The resolution describes the degree of aliasing that the design is subjected too, but the design generators are required to determine the exact aliasing structure of the design. The design is a resolution IV 2FF which means that the main effects are confounded with 3-factor interaction and 2-factor interactions are confounded with other 2-factor interactions as structured by the generators.

Table 4.3 lists all the experimental factor levels and experimental results for the VMD and Buildup responses. The runs were randomized in accordance with DoE best practice. The procedure and data master record is available as Appendix A.

Table 4.3: Screening DoE used for this Thesis and Results for the VMD and Build-up.[1]

Coded Factor in DX7®		**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**J**	**K**	**L**	**M**	**N**	**O**	**P**	**Q**	**Response:**	
Run Number:	Std No:	UPR	Mass TiO_2	Mass Styrene	Mass LMA	Mass DETA (Organic)	Mass Water	Mass PVOH Soln.	Mass HEC Soln.	Mass DETA (Aqueous)	Mass $FeSO_4$	Mass CHP	Initial Reactor Temperature	Stirrer Speed	Addition Rate	Emulsification Time	Stationary Period	Buildup	VMD
SCR-001	13	-10%	-25%	15%	20%	-20%	6%	10%	-10%	-20%	-20%	20%	30°C	330rpm	15min	10min	0min	1	43.71µm
SCR-002	31	-10%	25%	15%	20%	20%	-6%	-10%	-10%	20%	-20%	-20%	30°C	270rpm	15min	30min	0min	5	56.52µm
SCR-003	18	10%	-25%	-15%	-20%	20%	6%	10%	10%	-20%	-20%	-20%	30°C	270rpm	15min	30min	0min	0	36.31µm
SCR-004	33	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	22.5°C	300rpm	10min	20min	20min	1	41.31µm
SCR-005	1	-10%	-25%	-15%	-20%	-20%	-6%	-10%	-10%	-20%	-20%	-20%	15°C	270rpm	5min	10min	0min	0	55.37µm
SCR-006	22	10%	-25%	15%	-20%	20%	-6%	10%	-10%	20%	-20%	20%	15°C	270rpm	15min	10min	40min	5	11.13µm
SCR-007	35	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	22.5°C	300rpm	10min	20min	20min	2	44.93µm
SCR-008	7	-10%	25%	15%	-20%	-20%	-6%	10%	10%	-20%	20%	20%	15°C	270rpm	15min	30min	0min	1	28.12µm
SCR-009	2	10%	-25%	-15%	-20%	-20%	6%	10%	10%	-20%	20%	20%	15°C	330rpm	5min	10min	40min	0	35.41µm
SCR-010	32	10%	25%	15%	20%	20%	6%	10%	10%	20%	20%	20%	30°C	330rpm	15min	30min	40min	3	30.73µm
SCR-011	4	10%	25%	-15%	-20%	-20%	-6%	-10%	10%	20%	-20%	20%	30°C	330rpm	15min	10min	0min	0	28.45µm
SCR-012	26	10%	-25%	-15%	20%	20%	6%	-10%	-10%	20%	-20%	-20%	30°C	330rpm	5min	10min	40min	2	57.68µm
SCR-013	36	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	22.5°C	300rpm	10min	20min	20min	1	43.56µm
SCR-014	34	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	22.5°C	300rpm	10min	20min	20min	1	40.61µm
SCR-015	5	-10%	-25%	15%	-20%	-20%	6%	-10%	10%	20%	-20%	20%	30°C	270rpm	5min	30min	40min	1	37.27µm
SCR-016	28	10%	25%	-15%	20%	20%	-6%	10%	-10%	-20%	20%	-20%	15°C	330rpm	15min	10min	0min	5	28.98µm
SCR-017	37	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	22.5°C	300rpm	10min	20min	20min	0	44.68µm
SCR-018	17	-10%	-25%	-15%	-20%	20%	-6%	-10%	-10%	-20%	20%	20%	30°C	330rpm	15min	30min	40min	1	39.24µm
SCR-019	19	-10%	25%	-15%	-20%	20%	6%	10%	-10%	20%	-20%	20%	15°C	330rpm	5min	30min	0min	2	46.37µm
SCR-020	3	-10%	25%	-15%	-20%	-20%	6%	10%	-10%	20%	20%	-20%	30°C	270rpm	15min	10min	40min	0	66.03µm
SCR-021	29	-10%	-25%	15%	20%	20%	6%	10%	-10%	-20%	20%	-20%	15°C	270rpm	5min	30min	40min	5	73.13µm
SCR-022	6	10%	-25%	15%	-20%	-20%	-6%	10%	-10%	20%	20%	-20%	30°C	330rpm	5min	30min	0min	3	16.22µm
SCR-023	21	-10%	-25%	15%	-20%	20%	6%	-10%	10%	20%	20%	-20%	15°C	330rpm	15min	10min	0min	5	61.37µm
SCR-024	12	10%	25%	-15%	20%	-20%	-6%	10%	-10%	-20%	-20%	20%	30°C	270rpm	5min	30min	40min	1	41.02µm

[1] See Table C.3 for the uncoded values & Table C.4 for all the responses' results.

Coded Factor in DX7®		**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**J**	**K**	**L**	**M**	**N**	**O**	**P**	**Q**	**Response:**	
Run Number:	Std No:	UPR	Mass TiO_2	Mass Styrene	Mass LMA	Mass DETA (Organic)	Mass Water	Mass PVOH Soln.	Mass HEC Soln.	Mass DETA (Aqueous)	Mass $FeSO_4$	Mass CHP	Initial Reactor Temperature	Stirrer Speed	Addition Rate	Emulsification Time	Stationary Period	Buildup	VMD
SCR-025	15	-10%	25%	15%	20%	-20%	-6%	-10%	-10%	20%	20%	20%	15°C	330rpm	5min	10min	40min	5	44.19µm
SCR-026	25	-10%	-25%	-15%	20%	20%	-6%	10%	10%	20%	20%	20%	30°C	270rpm	5min	10min	0min	1	71.92µm
SCR-027	24	10%	25%	15%	-20%	20%	6%	-10%	-10%	-20%	20%	20%	30°C	270rpm	5min	10min	0min	1	42.29µm
SCR-028	11	-10%	25%	-15%	20%	-20%	6%	-10%	10%	-20%	20%	-20%	30°C	330rpm	5min	30min	0min	0	62.05µm
SCR-029	16	10%	25%	15%	20%	-20%	6%	10%	10%	20%	-20%	-20%	15°C	270rpm	5min	10min	0min	3	44.68µm
SCR-030	23	-10%	25%	15%	-20%	20%	-6%	10%	10%	-20%	-20%	-20%	30°C	330rpm	5min	10min	40min	5	13.53µm
SCR-031	14	10%	-25%	15%	20%	-20%	-6%	-10%	10%	-20%	20%	-20%	30°C	270rpm	15min	10min	40min	3	37.29µm
SCR-032	30	10%	-25%	15%	20%	20%	-6%	-10%	10%	-20%	-20%	20%	15°C	330rpm	5min	30min	0min	5	14.96µm
SCR-033	27	-10%	25%	-15%	20%	20%	6%	-10%	10%	-20%	-20%	20%	15°C	270rpm	15min	10min	40min	2	64.04µm
SCR-034	9	-10%	-25%	-15%	20%	-20%	-6%	10%	10%	20%	-20%	-20%	15°C	330rpm	15min	30min	40min	1	36.34µm
SCR-035	10	10%	-25%	-15%	20%	-20%	6%	-10%	-10%	20%	20%	20%	15°C	270rpm	15min	30min	0min	0	62.88µm
SCR-036	8	10%	25%	15%	-20%	-20%	6%	-10%	-10%	-20%	-20%	-20%	15°C	330rpm	15min	30min	40min	4	30.92µm
SCR-037	20	10%	25%	-15%	-20%	20%	-6%	-10%	10%	20%	20%	-20%	15°C	270rpm	5min	30min	40min	3	13.62µm

4.4 VMD Response Analysis

4.4.1 VMD Model Selection

Figure 4.2: Half-Normal Probability Chart for the VMD Response.

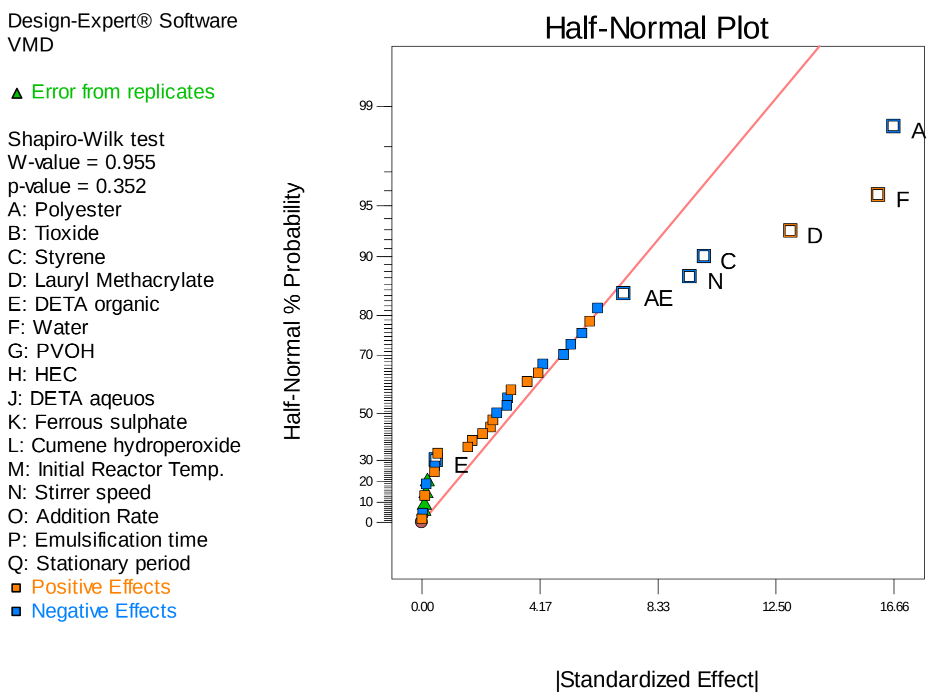
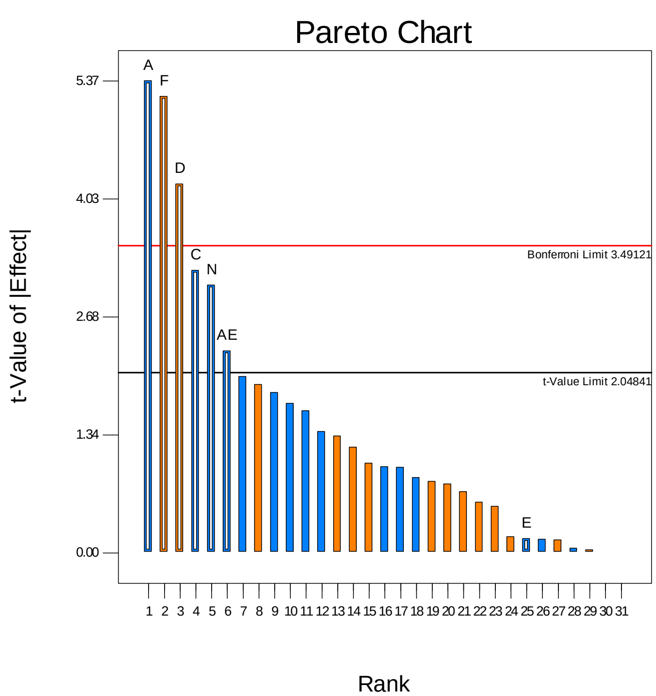


Figure 4.3: Pareto Chart for the VMD Response.



From Table 4.4, and Figure 4.2 & Figure 4.3 it can clearly be seen that the following factors have a significant influence on the VMD response (in descending order): (A) Mass UPR, (F) Mass Water, (D) Mass LMA, (C) Mass Styrene, (N) Stirrer Speed, (AE) 2nd order interaction between responses A & E, and (E) Mass DETA in the organic phase (needed for model hierarchy). The first three factors accounted for 58.04% of the effect contribution with the other significant factors accounting for 19.72% and the remaining factors being grouped in the error term accounting for 22.24% of the effect contribution.

Table 4.4: Modeled Effects and their Contribution for the VMD Response.

Type[1]	Term	Effect[2]	% Effect Contribution[3]
M	**A-Mass UPR**	**-16.66**	**22.78%**
E	B-TiO_2	-3.04	0.76%
M	**C-Mass Styrene**	**-9.98**	**8.17%**
M	**D-Mass LMA**	**13.03**	**13.93%**
M	**E-Mass DETA (organic)**	**-0.51**	**0.02%**
M	**F-Mass Water**	**16.12**	**21.33%**
E	G-Mass PVOH	-5.28	2.29%
E	H-Mass HEC	-6.22	3.18%
E	J-Mass DETA (Aqueous)	2.44	0.49%
E	K-Mass Ferrous sulphate	5.95	2.90%
E	L-Mass CHP	-3.02	0.75%
E	M-Initial Reactor Temp.	1.80	0.26%
M	**N-Stirrer speed**	**-9.47**	**7.35%**
E	O-Addition Rate	-0.48	0.02%
E	P-Emulsification Time	-5.02	2.07%
E	Q-Stationary Period	-4.29	1.51%
M	**AE**	**-7.14**	**4.18%**
E	Error Terms	-	7.76%

[1] M – indicates a factor included in the model; E – indicates a factor allocated to the error term.

[2] The effect is the change in the response as the factor changes from its low (-1) level to its high (+1) level

[3] The percentage effect contribution is sum of squares (see ANOVA) of the effect as a percentage of the total sum of squares for all the effects. The percentage effect contribution is only comparable if the effect terms have the same degrees of freedom.

Table 4.5: ANOVA Results for the VMD Response.[1]

Source	Sum of Squares	df	Mean SS	F-Value	p-value[2]
Model	7582.54	7	1083.22	14.04	**< 0.0001**
A-Mass UPR	2221.61	1	2221.61	28.80	**< 0.0001**
C-Mass Styrene	796.50	1	796.50	10.33	**0.0033**
D-Mass LMA	1358.12	1	1358.12	17.61	**0.0002**
E-Mass DETA (organic)	2.07	1	2.07	0.03	0.8712
F-Mass Water	2079.64	1	2079.64	26.96	**< 0.0001**
N-Stirrer speed	716.97	1	716.97	9.30	**0.0050**
AE – Interaction	407.62	1	407.62	5.28	**0.0292**
Curvature	8.48	1	8.48	0.11	0.7427
Residual	2159.63	28	77.13		
Lack of Fit	2144.21	24	89.34	23.16	**0.0038**
Pure Error	15.43	4	3.86		
Cor Total	9750.65	36			

Root MSE	8.78
Mean	41.81
C.V. %	21.01
PRESS	3836.03

R^2	0.778
Adj R^2	0.723
Pred R^2	0.607
Adeq Precision	14.95

Factor	Coefficient Estimate	df	Standard Error	95% CI – Low	95% CI - High
Intercept	41.62	1	1.55	38.44	44.80
A-Mass UPR	-8.33	1	1.55	-11.51	-5.15
C-Mass Styrene	-4.99	1	1.55	-8.17	-1.81
D-Mass LMA	6.51	1	1.55	3.33	9.69
E-Mass DETA (organic)	-0.25	1	1.55	-3.43	2.93
F-Mass Water	8.06	1	1.55	4.88	11.24
N-Stirrer speed	-4.73	1	1.55	-7.91	-1.55
AE – Interaction	-3.57	1	1.55	-6.75	-0.39
Centre Point	1.40	1	4.22	-7.25	10.05

The ANOVA indicates that the chosen model is significant as are the A, C, D, F, N & AE terms. The E term (Mass DETA in the organic phase) is not significant as was also observed in Figure 4.2 & Figure 4.3 however it is included to maintain the hierarchy of the model (AE is significant). The curvature of the model is not significant which suggests that the chosen design space is approximately linear. The model does not fit well as indicated by the significant lack of fit; however since this is only the screening phase this is not of concern as the model is not to be used for response predictions.

[1] For a full explanation of each term refer to Appendix D.

[2] Significant values in **Bold**

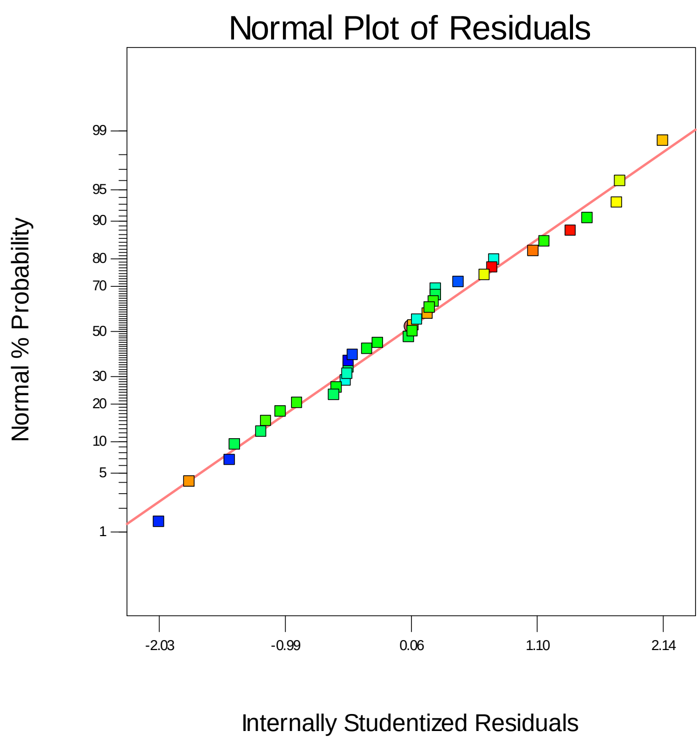
The fitted model[1] for the Volume Mean Diameter Response is as follows:

$$VMD = 41.62 - 8.33A - 4.99C + 6.51D - 0.25E + 8.06F - 4.73N - 3.57A \times E \qquad (4.2)$$

4.4.2 VMD Model Diagnostic

The following diagnostic methods were discussed in Chapter 3 – Table 3.1. The following figures are for the VMD model equation 4.2.

Figure 4.4: Normal Plot of Residuals for the VMD Response.



[1] The model is in coded units (-1 to 1) for comparison of modeled terms.

Figure 4.5: Residuals vs. Predicted Response for the VMD Response.

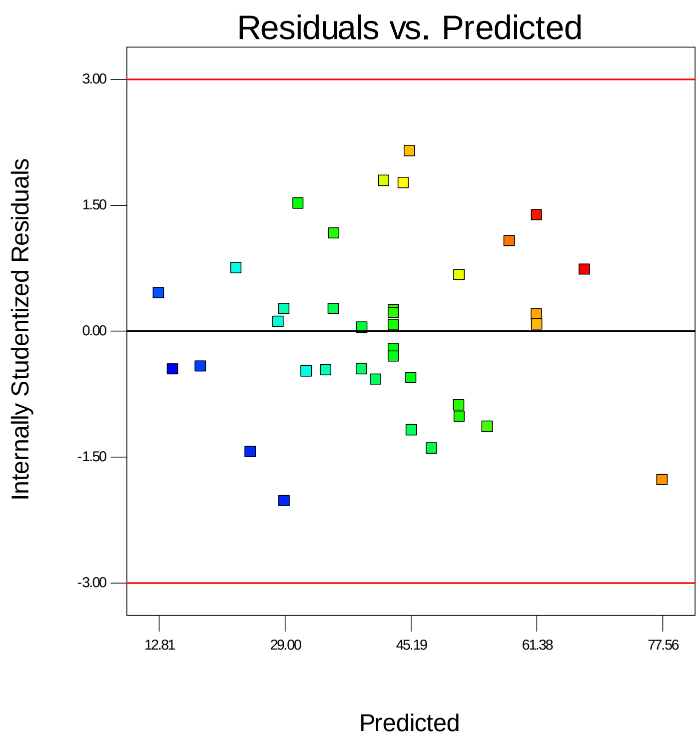


Figure 4.6: Residuals vs. Run Order for the VMD Response.

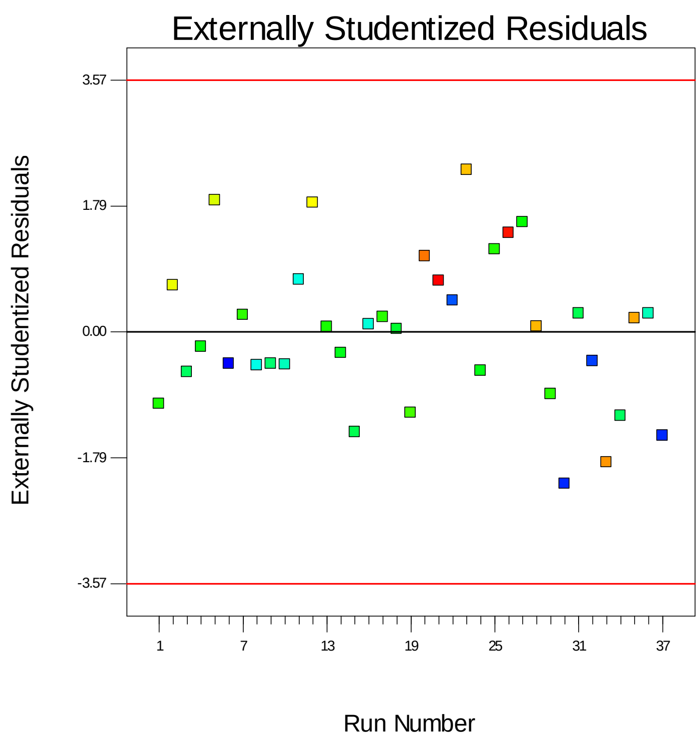


Figure 4.7: Cook's Distance for the VMD Response.

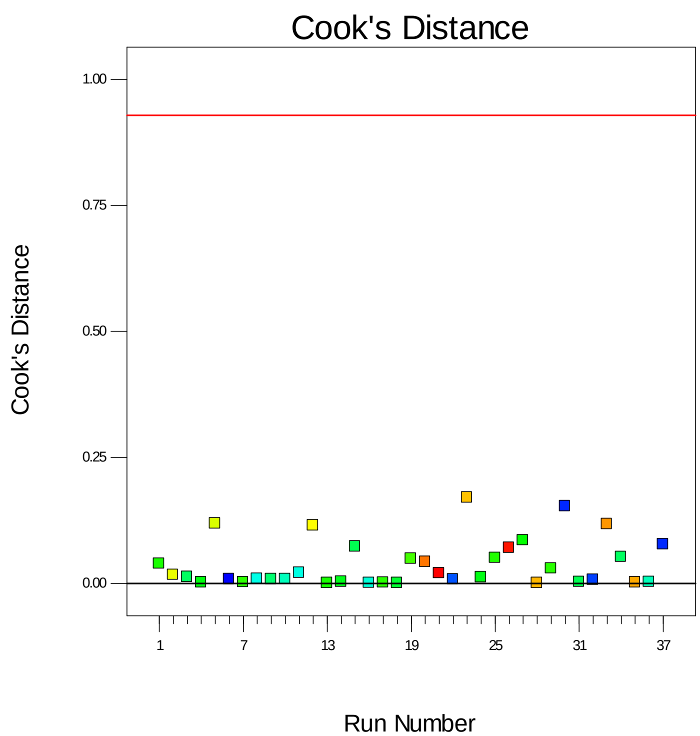
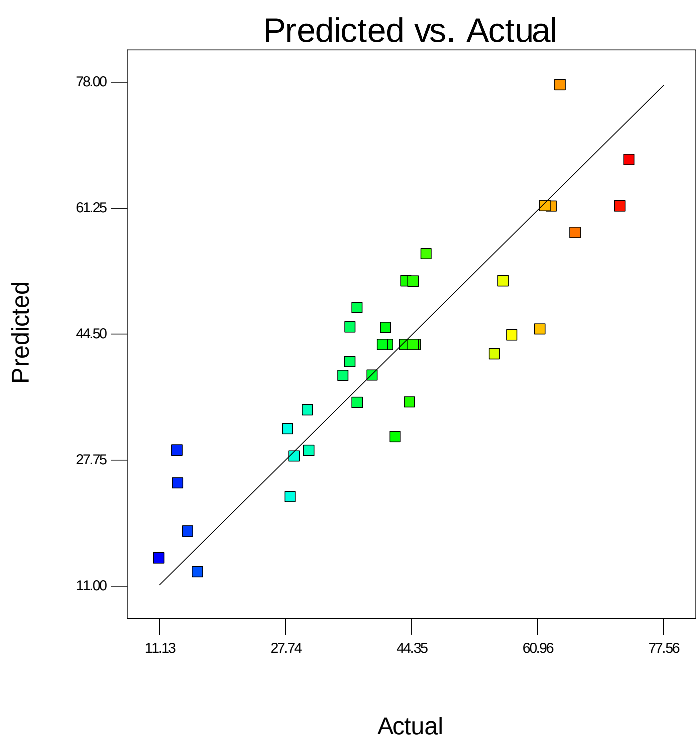


Figure 4.8: Predicted vs. Actual Response Plot for the VMD Response.



From Figure 4.4 it can clearly be seen that the residuals fall along a straight line and therefore the assumption of normality of the residuals is accepted. There are no observable trends in either Figure 4.5 or Figure 4.6 which indicates that the assumptions of sample independence and homoscedasticity are valid. None of the samples lie outside of the t-limits and none of the samples have excessive leverage over the model which suggests that there were no outliers in the data set.

Whilst in Figure 4.8 the data points do not fall along the 45° line they do follow a random pattern around the 45° line with no obvious problem regions. This most likely explains the significant lack of fit of the model but also graphically indicates that this is of little concern particularly since this is only the screening phase model and not the final predictive RPD model.

4.5 Buildup Response Analysis

4.5.1 Buildup Model Selection

Figure 4.9: Half-Normal Probability Chart for the Buildup Response.

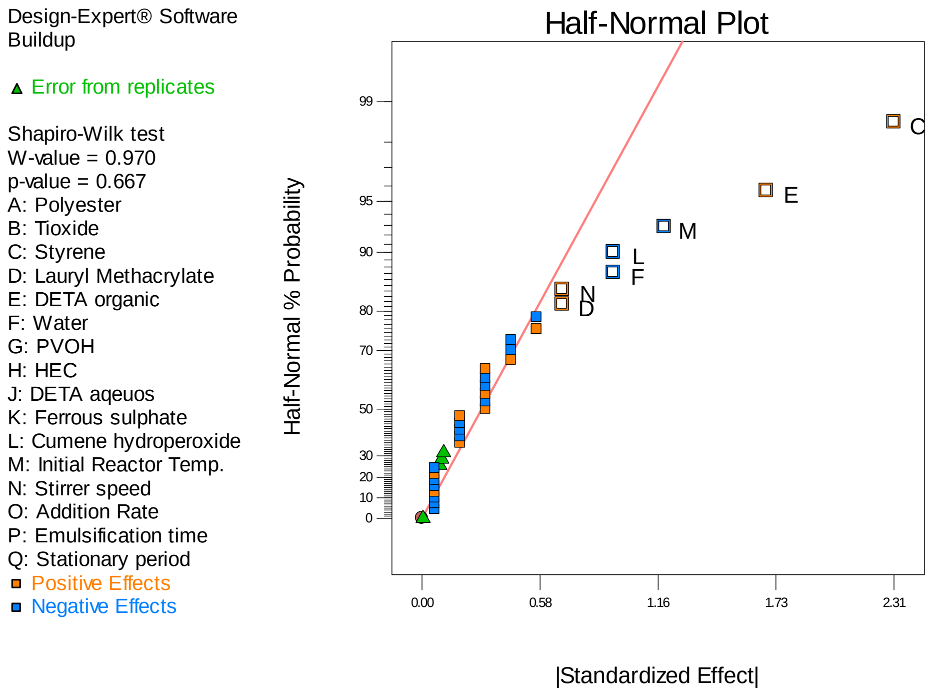
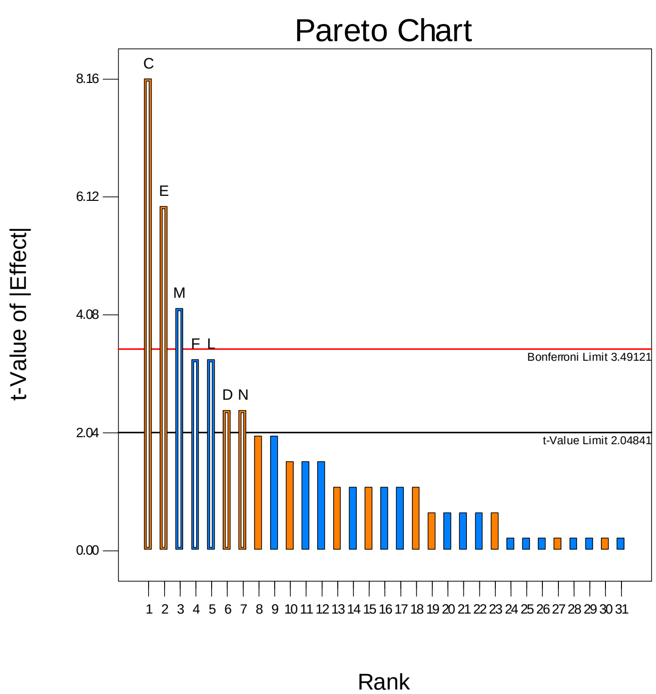


Figure 4.10: Pareto Chart for the Buildup Response.



From Table 4.6 and Figure 4.9 & Figure 4.10 it can clearly be seen that the following factors have a significant influence on the Buildup response (in descending order): (C) Mass Styrene, (E) Mass DETA in the Organic Phase, (M) Initial Reactor Temperature, (F) Mass Water, (L) Mass CHP, (D) Mass LMA, and (N) Stirrer Speed. The first two factors accounted for 53.06% of the effect contribution, with the other significant factors accounting for 32.32% and the remaining factors being grouped in the error term accounting for 14.62% of the effect contribution.

Table 4.6: Modeled Effects and their Contribution for the Build-up Response.

Type[1]	Term	Effect[2]	% Effect Contribution[3]
E	A-Mass UPR	0.19	0.23%
E	B-TiO_2	0.44	1.24%
M	**C-Mass Styrene**	**2.31**	**34.62%**
M	**D-Mass LMA**	**0.69**	**3.06%**
M	**E-Mass DETA (organic)**	**1.69**	**18.44%**
M	**F-Mass Water**	**-0.94**	**5.69%**
E	G-Mass PVOH	-0.06	0.03%
E	H-Mass HEC	-0.44	1.24%
E	J-Mass DETA (Aqueous)	0.31	0.63%
E	K-Mass Ferrous sulphate	-0.06	0.03%
M	**L-Mass CHP**	**-0.94**	**5.69%**
M	**M-Initial Reactor Temp.**	**-1.19**	**9.13%**
M	**N-Stirrer speed**	**0.69**	**3.06%**
E	O-Addition Period	-0.06	0.03%
E	P-Emulsification Period	-0.19	0.23%
E	Q-Stationary Period	0.56	2.05%
E	Error Terms	-	14.62%

[1] M – indicates a factor included in the model; E – indicates a factor allocated to the error term.
[2] The effect is the change in the response as the factor changes from its low (-1) level to its high (+1) level.
[3] The percentage effect contribution is sum of squares (see ANOVA) of the effect as a percentage of the total sum of squares for all the effects. The percentage effect contribution is only comparable if the effect terms have the same degrees of freedom.

Table 4.7: ANOVA Results[1] for the Buildup Response.

Source	Sum of Squares	df	Mean SS	F-Value	p-value[2]
Model	98.46875	7	14.07	21.88	< 0.0001
C-Mass Styrene	42.78125	1	42.78	66.55	< 0.0001
D-Mss LMA	3.78125	1	3.78	5.88	0.0220
E-Mass DETA (organic)	22.78125	1	22.78	35.44	< 0.0001
F-Mass Water	7.03125	1	7.03	10.94	0.0026
L-Mass CHP	7.03125	1	7.03	10.94	0.0026
M-Initial Reactor Temp.	11.28125	1	11.28	17.55	0.0003
N-Stirrer Speed	3.78125	1	3.78	5.88	0.0220
Curvature	7.0988176	1	7.10	11.04	0.0025
Residual	18	28	0.64		
Lack of Fit	16	24	0.67	1.33	0.4323
Pure Error	2	4	0.50		
Cor Total	123.56757	36			

Root MSE	0.8
Mean	2.11
C.V. %	38.03
PRESS	31.57

R^2	0.845
Adj R^2	0.807
Pred R^2	0.745
Adeq Precision	16.6

Factor	Coefficient Estimate	df	Standard Error	95% CI - Low	95% CI – High
Intercept	2.28	1	0.14	1.99	2.57
C-Mass Styrene	1.16	1	0.14	0.87	1.45
D-Mss LMA	0.34	1	0.14	0.05	0.63
E-Mass DETA (organic)	0.84	1	0.14	0.55	1.13
F-Mass Water	-0.47	1	0.14	-0.76	-0.18
L-Mass CHP	-0.47	1	0.14	-0.76	-0.18
M-Initial Reactor Temp.	-0.59	1	0.14	-0.88	-0.30
N-Stirrer Speed	0.34	1	0.14	0.05	0.63
Centre Point	-1.28	1	0.39	-2.07	-0.49

The ANOVA indicates that the chosen model is significant as are the C, D, E, F, L, M, & N terms. The curvature of the model is significant which suggests that the chosen design space will require a non-linear response surface model for the RPD model development. The lack of fit was insignificant which indicates that all the important factors have been selected.

The fitted model[3] for the Buildup Response is as follows:

$$Buildup = 2.28 + 1.16C + 0.34D + 0.84E - 0.47F - 0.47L - 0.59M + 0.34N \tag{4.3}$$

[1] For a full explanation of each term refer to Appendix D.

[2] Significant Values in Bold.

[3] The model is in coded units (-1 to 1) for comparison of modeled terms.

4.5.2 Buildup Model Diagnostic

The following diagnostic methods were discussed in Chapter 3 – Table 3.1. The following figures are for the Buildup model equation 4.3.

Figure 4.11: Normal Plot of Residuals for the Buildup Response.

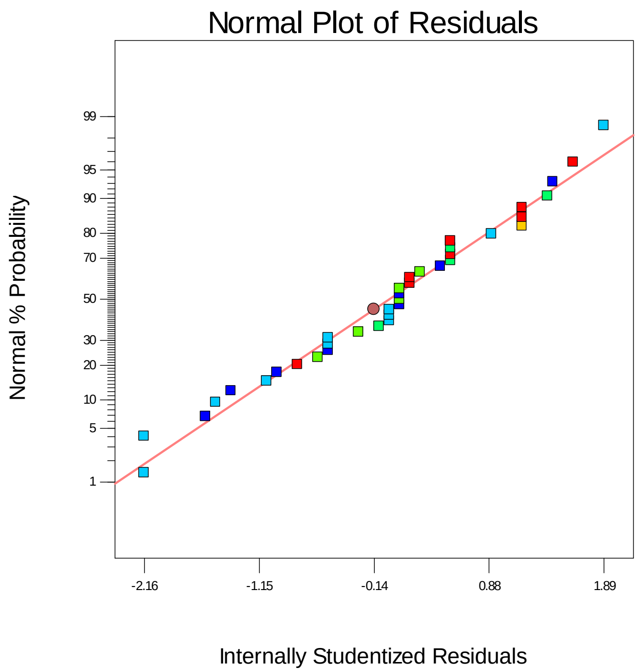


Figure 4.12: Residuals vs. Predicted Response for the Buildup Response.

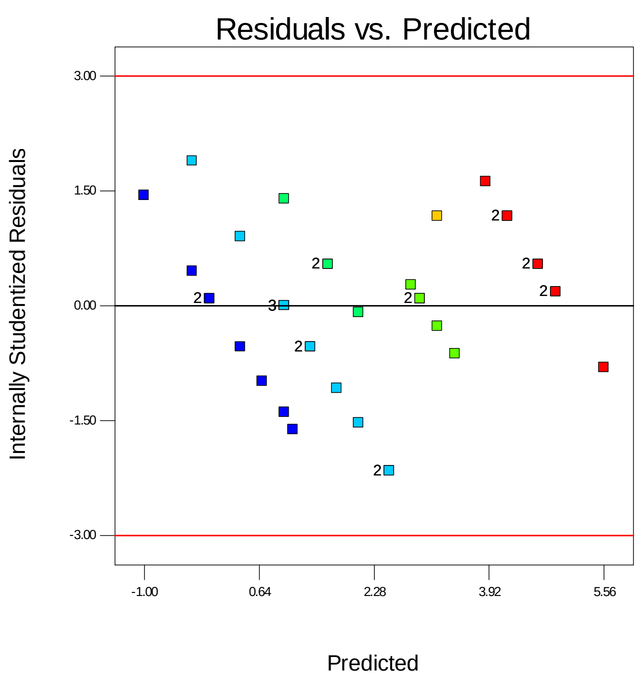


Figure 4.13: Residuals vs. Run Order for the Buildup Response.

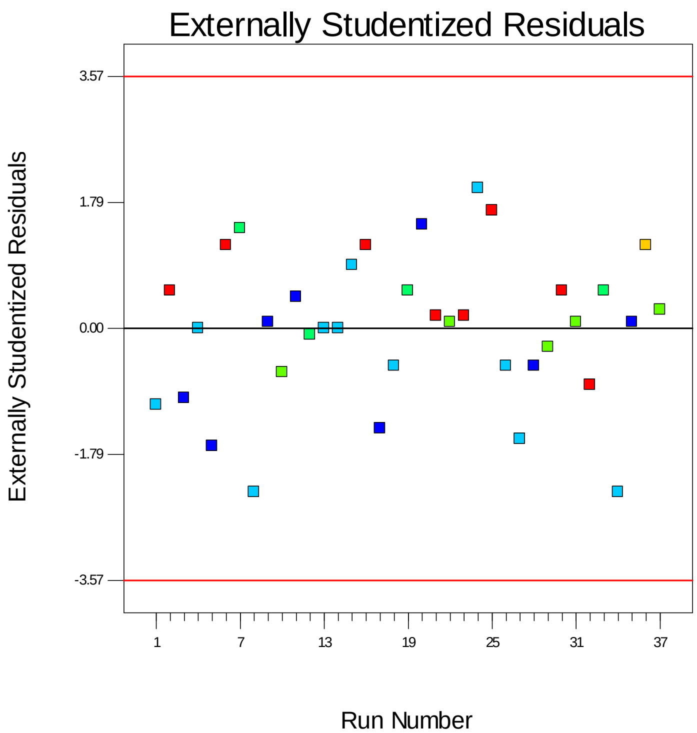


Figure 4.14: Cook's Distance for the Buildup Response.

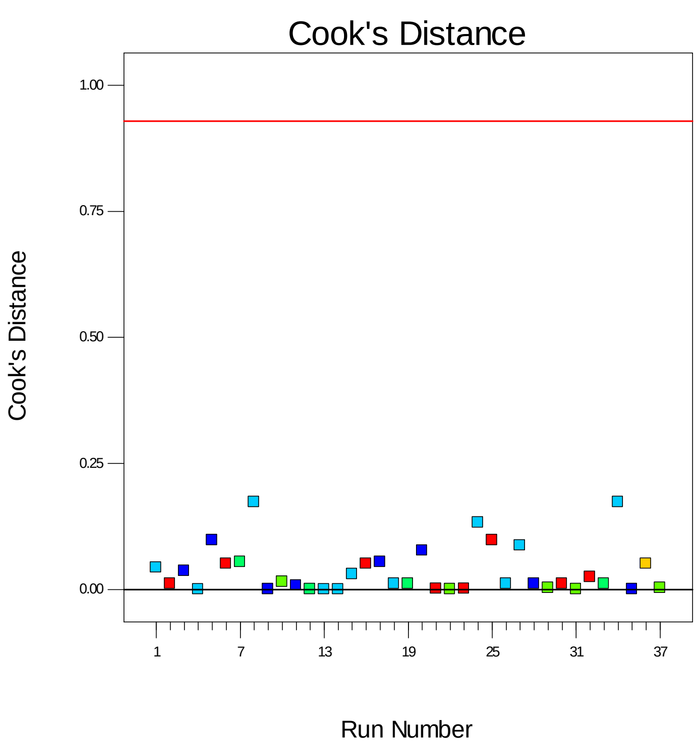
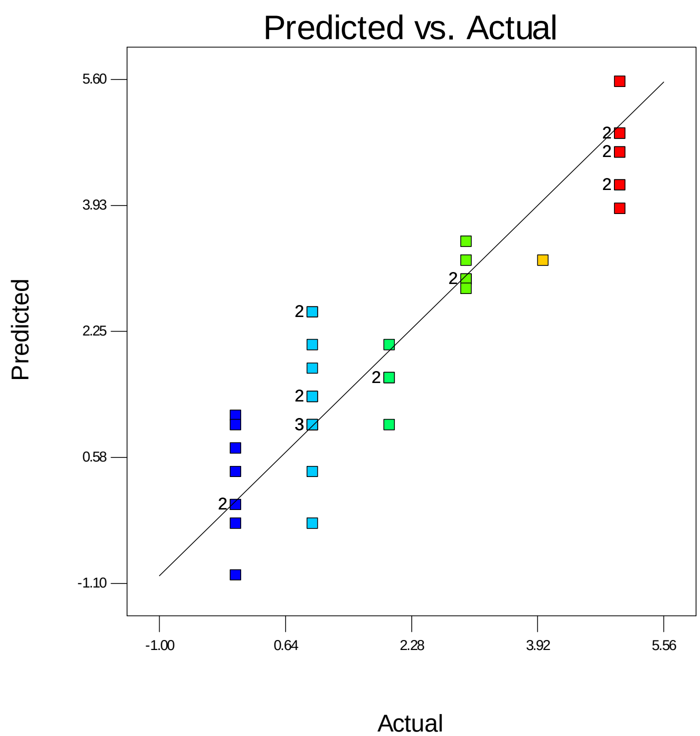


Figure 4.15: Predicted vs. Actual Response Plot for the Buildup Response.



From Figure 4.11 it can be clearly seen that the residuals fall along a straight line and therefore the assumption of normality of the residuals is accepted. There are no observable trends in either Figure 4.12 or Figure 4.13 which indicates that the assumptions of sample independence and homoscedasticity are valid. None of the samples lie outside of the t-limits and none of the samples have excessive leverage over the model which suggests that there were no outliers in the data set. In Figure 4.15 the data points fall approximately along the 45° line. The stratified appearance in Figure 4.12 & Figure 4.15 is due to the discrete nature of the response.

4.6 Model Interpretation

A detailed quantitative interpretation of the results is premature at this stage of the thesis; however a general interpretation of the screening phase results is warranted. It is also best practice to compare the results of any DoE to previous experimentation and theory, since if the DoE conclusions drawn are contradictory or largely dissimilar to the previous knowledge of the system this should red flag the DoE and all new conclusions drawn should only be made with great care. (Unfortunately if the conclusions are in agreement this does not mean that all new conclusions can be considered to be accurate but it does put the odds in your favour).

4.6.1 Interpretation of the VMD Model

The VMD model selection and validation has already been discussed in section 4.4. From the ANOVA results for the VMD (Table 4.5) the following interpretation of the model can be made:

The model is clearly significant with only a 0.01% chance that this result was due to noise. There is significant lack-of-fit (variation of the data around the model) for the model which means that the model does not fit all of the data points well. The amount of variation around the mean explained by the model is acceptable (R^2 = 0.778). However, the predicted variation of the response data explained by the model is low (Pred R^2 = 0.607) and therefore the model should not be relied upon for accurate predictions. This is however acceptable since the model is only for screening of the significant variables.

The model indicated that the quantity of UPR and quantity of the styrene were determined to have a significant effect on the particle size. This was expected since the particle size in a suspension polymerisation is known to be affected by the fraction hold-up, viscosity & density of the dispersed (organic) phase and the interfacial tension between the phases, (Langner et. al., 1980); all of which are affected by the levels of UPR and styrene.

The quantity of LMA has previously been determined to affect the particle size (Engelbrecht et. al., 2006) with the particle size increasing with increased levels of LMA this was confirmed by the screening experiments conducted here.

The quantity of DETA added to the organic phase was not considered to be significant by the screening DoE. However the interaction between the quantity of the UPR and the quantity of DETA in the organic phase was significant. The proposed mechanism for the interaction was that the polyamine (DETA) partially ionises the carboxyl end groups of the UPR as follows:

$$R - COOH + R' - NH_2 \Longleftrightarrow R - COO^- + R' - NH_3^+$$

This interaction is believed (Terblanche, 2002) to cause the UPR chains to orientate creating a more stable macro-molecular structure. This partial ionisation also aids with the formation of a stable liquid-liquid suspension. This fits well with the mechanism for vesicle formation proposed by Gous (2003) which indicates that the DETA is critical for the vesicle formation particularly the size and quantity of the vesicles. The more vesicles form, and the larger the vesicles become, the more the particle will swell during the droplet formation and therefore, hypothetically, the larger the particle size. This seems to be the case since as already stated the DETA × UPR interaction has a significant effect on the VMD.

The quantity of water added to the aqueous phase was determined to have a significant effect on the VMD. This was expected since the level of water will have an effect on the hold-up, viscosity & density of the continuous (aqueous) phase and the interfacial tension between the phases. A similar result was found in the work conducted by Terblanche (2002). Terblanche found that adding additional water to the initial quantity of water increased the average particle size; the same observation during the screening experimentation for which a significant positive effect[1] of the quantity of water on the VMD was found.

Finally the stirrer speed was determined to have a significant effect on the VMD. This result is supported by both the developmental work by Terblanche (2002) on the MVP product and the theory of the mechanisms for breakage and coalescence of the droplets in a suspension polymerisation where the mixing provides the required energy (Koutoulas & Kiparissides, 2006).

As to the non-significant factors, Terblanche (2002) found that the emulsification time did have a significant effect on the PSD but only to a maximum of 20minutes at which point it is believed that the PSD reaches its dynamic equilibrium and then according to Jahanzad et. al (2005) the PSD remains constant. Therefore it is expected that the emulsification time has no statistically significant effect since at the factor levels chosen the PSD should have reached dynamic equilibrium.

Terblanche (2002) also indicated that the emulsification temperature had no significant effect on the PSD below 27°C, but the MVP PSD increased exponentially above this temperature. As with the emulsification time the levels chosen for the temperature in the screening experiment were in the temperature range which had no significant effect.

4.6.2 Interpretation of the Buildup Model

The Buildup model selection and validation has already been discussed in chapter 4.5. The effects of parameters on the buildup response is more difficult to interpret and explain than for the VMD due to the complex and poorly understood mechanisms involved. However from the ANOVA Results for the Buildup (Table 4.7) the following interpretation of the model can be made:

The model is clearly significant with only a 0.01% chance that this result was due to noise. The curvature of the model is significant which suggests that the Build-up response is not linear and therefore, to accurately model the response a non-linear model will be required. The amount of variation around the mean explained by the model is good (R^2 = 0.845). Even with the significant curvature of the response, the predicted variation of the data explained by the model is acceptable (Pred R^2 = 0.745).

The model indicated that an increase in the styrene level leads to an increase in the buildup (positive effect). From a physical perspective this is possibly due to the increased hold-up in the reactor; from a chemical perspective, the styrene monomer acts as a grafting monomer between the PVOH and / or HEC with the UPR (Paine, 1990; de Wet Roos, *personal communication*, 26 July 2010).

A similar case can be made for the LMA. Since an increase in the LMA concentration is known to coarsen the particle size, the effective holdup is increased and therefore the viscosity increases.

[1] Increase in factor causes an increase in the response.

The DETA increases the water pickup (vesiculation) of the organic droplets (Gous, 2003). This increases the effective hold-up ratio. This has the effect of concentrating the droplets (particles) which in turn increases the suspensions viscosity and the build-up in the reactor as the suspension is less likely to flow. The DETA may also draw the styrene monomer into the aqueous phase increasing the chance that grafting will occur with the PVOH & HEC (Paine, 1990; de Wet Roos, *personal communication*, 26 July 2010).

An increase in the quantity of the water reduces the droplet concentration in the suspension and the viscosity of the suspension. The increase in water reduces the concentration of the PVOH & HEC in the aqueous phase, reducing the probability of grafting in the aqueous phase as well as reducing the influence of the grafted polymers on the overall viscosity buildup.

The radicals formed from the CHP have a tendency to breakdown the PVOH & HEC polymer chains having an overall reduction in the chain length of the PVOH & HEC polymer molecules (Rowe, 1978; de wet Roos, *personal communication*, 26 July 2010). The reduction in the size of these polymer chains will have an overall effect of reducing the viscosity of the aqueous phase as well as the buildup in the reactor. The reduction in the chain size reduces the shear thinning response of the aqueous phase and hence reduces the buildup in the reactor. Hence an increase in the CHP concentration reduces the overall buildup in the reactor.

The initial reactor temperature is known to affect the water pickup (vesiculation) of the MVP. In previous experiments the contrast ratio has been observed to increase with a decrease in temperature (Terblanche, 2002; Clarke, 2009) which indicates a higher amount of vesiculation within the particles (Observed again in these experiments). The increase in vesiculation reduces the continuous phase volume and increases the effective holdup, this in turn increases the suspensions viscosity and the probability that buildup will occur.

In addition to the influence of the temperature on the vesicle formation, the kinetics of any chemical reaction are known to be temperature dependent and in general are dependent on the temperature to differing degrees. Thus, depending on what temperature the reactions occur at, a different reaction may be favoured. Thus hypothetically based on the screening experiment's buildup model those reactions favouring buildup are faster, and hence will occur more frequently, at lower temperatures than the competing reactions which are favoured at higher temperatures. It should also be noted that the mass transfer is also temperature dependant; unfortunately due to the lack of knowledge of the reaction kinetics and the mass transfer of the system it cannot be determined which is the rate limiting process, hence only the empirical observation of these effects can be stated and a hypothesis proposed.

4.6.3 Summative Interpretation of Correlation between the Responses

The dependency of the suede paint properties on the Suede MVP is not well understood particularly with regards to determining the suede effect or the effect on the colour development. The suede effect is particularly difficult to determine due to the subjective nature of the effect.

A study of the correlation between the responses was done to determine any dependencies of interest particularly between the suede paint properties (colour and suede effect) and the properties of the Suede MVP. Strong correlations between any of the properties would help to better specify the Suede MVP and improve the focal point for the optimisation of the MVP.

The correlation matrix (Table 4.8) is a summative table of the Pearson Correlation Coefficients (equation 4.4) for the screening DoE's Response variables conducted using the Statistica® Software. The MVP characteristic responses' correlation to the suede paint characteristics (Coarseness & Tint Strength) can be used to determine which Suede MVP characteristics give the best indication of the Suede MVP's performance in the suede paint.

$$r_{xy} = \frac{s_{xy}}{s_x s_y} = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}(y_i - \bar{y})^2}} \quad (4.4)$$

The Pearson Correlation Coefficient has a value between -1 to 1 which can be interpreted as:

$r_{xy} = 1$: 100% positive correlation.

$r_{xy} = -1$: 100% negative correlation.

$r_{xy} = 0$: No correlation.

The correlations between the responses are listed in Table 4.8. Each correlation between the responses was subjected to a statistical significance test, the correlations in red are significant at the 95% significance level and the correlations of interest are highlighted in blue.

Table 4.8: Correlations[1] for the Screening Responses.

	Buildup	SG	%NVC	SMD	VMD	SDevS	SDevV	Viscosity	CR	CV (SMD)	CV (VMD)	Coarseness[2]	Tint Strength (Average)[3]
Buildup	1.00	-0.49	0.34	-0.49	-0.27	-0.25	-0.14	0.54	0.35	0.44	0.47	-0.20	-0.25
SG	-0.49	1.00	0.13	0.11	-0.23	-0.27	-0.34	-0.54	0.22	-0.61	-0.36	-0.31	0.34
%NVC	0.34	0.13	1.00	-0.38	-0.51	-0.55	-0.54	-0.31	0.22	-0.18	-0.16	-0.51	0.42
SMD	-0.49	0.11	-0.38	1.00	0.86	0.79	0.71	-0.06	-0.19	-0.42	-0.47	0.71	0.11
VMD	-0.27	-0.23	-0.51	0.86	1.00	0.99	0.96	0.29	-0.19	0.09	-0.13	0.92	-0.18
SDevS	-0.25	-0.27	-0.55	0.79	0.99	1.00	0.98	0.34	-0.19	0.19	-0.04	0.93	-0.22
SDevV	-0.14	-0.34	-0.54	0.71	0.96	0.98	1.00	0.43	-0.14	0.31	0.12	0.93	-0.31
Viscosity	0.54	-0.54	-0.31	-0.06	0.29	0.34	0.43	1.00	0.32	0.57	0.50	0.31	-0.61
CR	0.35	0.22	0.22	-0.19	-0.19	-0.19	-0.14	0.32	1.00	-0.05	0.23	-0.11	0.16
CV (SMD)	0.44	-0.61	-0.18	-0.42	0.09	0.19	0.31	0.57	-0.05	1.00	0.73	0.25	-0.55
CV (VMD)	0.47	-0.36	-0.16	-0.47	-0.13	-0.04	0.12	0.50	0.23	0.73	1.00	0.03	-0.53
Coarseness	-0.20	-0.31	-0.51	0.71	0.92	0.93	0.93	0.31	-0.11	0.25	0.03	1.00	-0.19
Tint Strength (ave)	-0.25	0.34	0.42	0.11	-0.18	-0.22	-0.31	-0.61	0.16	-0.55	-0.53	-0.19	1.00

[1]Correlations in Red are considered to be significant at the 95% significance level.

[2]Qualitative Visual rating (0-5) 0 being very fine and 5 being very coarse. Measured on the suede paint produced from the MVP.

[3]*CRGI Test Method 73* (*sinne anno).* Measured on the suede paint produced from the MVP.

The following correlations are worth noting:

> The particle size distribution (PSD) variables of the Suede MVP, particularly the VMD (0.92), correlate well with the Coarseness of the suede paint appearance. Therefore the volume mean diameter (VMD) should be used to specify the PSD of the Suede MVP. Previously the PSD was specified using the Number average particle size. However, during this study and other work conducted by this author (Clarke, 2009) it was found that the VMD characterised the PSD of the Suede MVP the best.
>
> The coefficient of variance for the VMD (The SDevV divided by the VMD as a percentage) has a significant but average correlation with the Tint Strength. This indicates that the relative spread (independent of the mean) of the particle size distribution affects the colour development of the paint. This effect is focused on the lightness of the paint and has a significant influence on the tint strength of the paint base.

It is essential that the specifications of the MVP characteristics are relevant to its application as optimisation of non-relevant characteristics will have no commercial value. Therefore the above findings are of critical importance as the value of the Suede MVP is in its influence on the suede effect in paint. As a result the VMD of the Suede MVP should be optimised to achieve the desired suede effect (Coarseness) of the suede paint. The variation exhibited by the coefficient of variation, should be minimised to reduce the colour development variation experienced by the suede paint between batches of Suede MVP.

4.7 Screening Phase Conclusion

The conclusions drawn from the interpretation of the model and the experimental results are either supported by literature or by previous experimental work. None of the conclusions drawn were quantitative since this phase of the experimentation was for screening of the significant variables only; therefore experimental validation will not be conducted at this stage of the investigation but will be conducted on the optimisation model only.

To summarise the following variables are considered to be significant for the two responses and will be investigated further in Chapter 5:

1. Quantity of UPR.
2. Quantity of Styrene.
3. Quantity of Lauryl Methacrylate.
4. Quantity of DETA added to the organic phase.
5. Quantity of water.
6. The Stirrer Speed.
7. The Initial Reactor Temperature.

Whilst the CHP did have a small (< 6%) yet significant effect on the Buildup it had none on the VMD. It will therefore be left out of the optimisation phase of the experiments to keep the number of factors to a manageable level.

In the beginning of this section it was mentioned that the batch-to-batch variation of the UPR had a significant influence on the final characteristics of the MVP product. Therefore the UPR batch-to-batch variation will be included as an 8^{th} & 9^{th} variables in the next phase of the experimentation as:

8. UPR Acid Value
9. UPR Brookfield Viscosity

The next phase of this Thesis will be to optimise the formulation and ensure that the process is as robust as possible to the batch-to-batch variation of the UPR. This work will be covered in chapter 5.

4.8 Nomenclature

Latin Variable	**Description**	**Units**
A	Mass UPR	-
B	Mass TiO_2	-
C	Mass styrene	-
D	Mass LMA	-
E	Mass DETA (Organic)	-
F	Mass water	-
G	Mass PVOH Soln.	-
H	Mass HEC Soln.	-
J	Mass DETA (Aqueous)	-
K	Mass ferrous sulphate	-
L	Mass CHP	-
M	Initial reactor temperature	-
N	Stirrer speed	-
O	Addition Rate	-
P	Emulsification time	-
Q	Stationary period	-
r	Pearson Correlation Coefficient	-
S	Sample covariance	-
X	Factor value	-
Y	Response variable	-
Greek Variables	**Description**	**Units**
B	Factor regression coefficient	-
E	Error	Unspecified

Subscript	**Description**	**Subscript**	**Description**
0	Mean	i, j,	Generic reference
x, y	Variable reference		

5 Modelling and Optimisation Utilising Statistical Methods

5.1 Introduction

It has frequently been observed that the unsaturated polyester (UPR) has a significant influence on the final characteristics of the Suede MVP. The sensitivity of the MVP to the UPR has made it impossible for any new batch of UPR to be used directly in an industrial scale batch of MVP before testing in the lab. Any batch-to-batch variation in the UPR has a compounded effect when the variation is propagated through to the MVP properties.

Robust Parameter Design (RPD) offers the process engineer, the opportunity to develop an optimised formulation & process for a product that will ensure that the product is as robust to input variation as possible whilst still achieving the products desired properties.

The objectives of the RPD Model are to:

1. Develop a second-order empirical model for the MVP process for formulation design.
2. Develop a robust optimised process by reducing the dispersion effect of the UPR noise variable, through manipulation of control variables.
3. Build a model which can be used to predict operating conditions which mitigate the influence of the UPR and results in a product consistently meeting the required specifications.
4. The model should allow for the prediction of formulation & processing conditions of the MVP system to develop new robust products to meet specific product characteristics as required by the user.

It was previously mentioned in Chapter 4 that a Screening DoE such as the 2-level fractional factorial (2^{16-11}) whilst useful for finding significant effects as economically as possible, suffers from the drawback of not being able to optimise a process, especially in the case of non-linear responses. Therefore a non-linear model was developed for optimisation of the process.

The experiments where run on the 2L scale[1] due to the small quantities of the UPR[2]. Geometric similarity of the vessels was kept and the mixer speed was adjusted in accordance with the batch scaling work previously conducted by the author (Clarke 2009b) who found that the batches could be scaled without any statistically significant difference in the properties and well within acceptable batch-to-batch variation limits.

[1] compared to the screening design which was run on the 5L scale

[2] A maximum of 15kg was available for each of the UPR batches produced in the lab due to the difficulties with accurately reproducing the UPR batches.

5.2 The Design

5.2.1 Experimental Factors

The factors that were screened in Chapter 4 were categorised as either significant or non-significant based upon their influence on the responses. The two additional responses, UPR Acid Value & Viscosity were added and the factor levels where determined for the RPD model experimentation. The factors with their screening DoE and RPD DoE levels are listed in Table 5.1.

Table 5.1: Factors and Factor Levels for the Design of Experiments.

Number	**Factor**	**Screening Levels**		**RPD RSM Levels**	
Significant Factors		**Low**	**High**	**Low**	**High**
1	Mass UPR	-10%	+10%	**-13%**	**+13%**
2	Mass Styrene	-15%	+15%	-15%	+15%
3	Mass LMA	-20%	+20%	-20%	+20%
4	Mass DETA (Organic)	-20%	+20%	-20%	+20%
5	Mass Water	-6%	+6%	-6%	+6%
6	Stirrer Speed[1]	270rpm	330rpm	**250(300)rpm**	**350(400)rpm**
7	Initial Reactor Temperature	15°C	30°C	15°C	30°C
New Factors (Polyester Characteristics)					
8	Acid Value	NA	NA	24.65 $mgKOH.g^{-1}$	47.84 $mgKOH.g^{-1}$
9	Viscosity	NA	NA	1880cP	2273cP
Non-Significant Factors		**Low**	**High**	**Chosen Level**	
10	Mass TiO_2	-25%	+25%	0%	
11	Mass PVOH	-10%	+10%	0%	
12	Mass HEC	-10%	+10%	0%	
13	Mass DETA (Aqueous)	-20%	+20%	0%	
14	Mass Ferrous Sulphate	-20%	+20%	0%	
15	Mass CHP	-20%	+20%	0%	
16	Addition Rate	5min	15min	10min	
16	Emulsification Time	10min	30min	20min	
18	Stationary Period	0min	40min	**0min**	

The justification for each factor level choice is as follows:

1. **Mass UPR** – This was increased to ±13% which is approximately ±2% of the total formulation. This is the maximum acceptable variation of the UPR since any less would result in too low a %NVC and any more could result in inversion of the product.
2. **Mass Styrene** - Kept at ±15% due to influence on Build-up. Approx. ±0.87% of total formulation.
3. **Mass LMA** – The levels are kept at ±20% to avoid too extreme conditions.
4. **Mass DETA (Organic)** – No change to levels as already the variation (±20%) is high and more than the polyester (±13%) variation.

[1] Speeds in parenthesis are for the 2L scale.

5. **Mass Water** – No Change as this is already ±3% of the total formulation and therefore ±3% on %NVC.
6. **Stirrer Speed** – The region has been expanded to increase the experimental design space.
7. **Initial Reactor Temperature** – Primarily affects the contrast ratio (believed to be through vesicle formation) would ideally be as low as possible. The levels were selected to remain the same as the screening levels.
8. **Acid Value** – These acid values are outside the product specification range and were determined by the limits of reproducing the batches in sufficient quantity for the experimentation.
9. **Viscosity** – The viscosities are outside the product specification range and were determined by the limits of reproducing the batches in sufficient quantity for the experimentation.
10. **Mass TiO_2** – Primarily influences the colour development of the paint (Tint Strength) and therefore it is kept at the current level.
11. **Mass PVOH** – Affects the %NVC and SDev minimally (<5%). The 0% level was chosen since the water level can be used to influence the PVOH% strength. The ratio of PVOH & HEC is fixed.
12. **Mass HEC** – Affects the %NVC and SMD minimally (~5%). The 0% level was chosen since the water level can be used to influence the HEC% strength. The ratio of PVOH & HEC is fixed.
13. **Mass DETA (Aqueous)** – Had no significant effect on anything. Therefore it will be kept at the 0% level for neutralisation.
14. **Mass Ferrous Sulphate** – Did not have a significant effect on any of the important characteristic of the Suede MVP. The 0% level will be used to keep the ratio to CHP the same.
15. **Mass CHP** – Affects the free monomer. This may need to be adjusted to reduce the free monomer for the new formulation. (Kept at 0% for this thesis).
16. **Addition Rate** – Had no significant effect. 10minutes was chosen as it is a reasonable standard achieved at the plant.
17. **Emulsification Time** – Selected to remain at 20min as this is the point when dynamic equilibrium for the batch has been determined to be reached (Terblanche, 2002).
18. **Stationary Period** – The Screening DoE results indicated that the stationary period had no significant effect on any of the responses. This is supported by literature where it was suspected that the incorporation of the stationary period to the process may not be necessary (Theron, 2000; Engelbrecht, 2002); the stationary period was initially added to the process based on the initiator system theory. Since it was found to have no significant effect, the 0min level was chosen to reduce the overall processing time.

5.2.2 Managing the Unsaturated Polyester Resin

Two of the UPR batches (A & B) were procured from the UPRs' supplier. These batches were within specification for the acid value but had significantly differing viscosities. To complete the design space two additional UPRs where manufactured[1] in accordance with the work by Simpson (2010) for a higher acid value but with viscosities comparable to the original batches.

Table 5.2: UPR Properties.

Batch	Acid value /mg KOH.g^{-1}	Viscosity @ 25°C Brookfield /cP	Viscosity @ 25°C Gardner–Holdt	%NVC	SG @ 25°C
Specification[2]	24 – 28		T - U	66 - 68	1.09 – 1.13
A	32.44	2166	V	66.32%	1.108
B	24.65	1896	U-V	65.81%	1.101
C	47.88	1880	U-V	66.77%	1.116
D	47.84	2273	V	68.34%	1.098
Verification Batches					
E	26.41	1809	U	69.23%	1.106
F	27.12	1928	U-V	68.94%	1.118

Therefore UPR was only available at the 4 extreme points of the UPR design space. This proposed a problem for developing a D-optimal nonlinear experimental design for the design space. This constraint resulted in a design of slightly lower power for the UPR design factors. The additional disadvantage to the design was that the quadratic terms of the UPR characteristic factors are confounded with the intercept of the model – This was deemed acceptable since the UPR was treated as a noise variable and the noise quadratic terms are generally ignored in a RPD analysis.

It is virtually impossible to manufacture UPRs that spans the design space orthogonally since the acid value & viscosity of the polyesters co-vary. The UPRs were also manufactured to be as close to the specified value as possible but with minor deviations that were not catered for in the model but was deemed acceptable since the UPR will be treated as a noise and not a control variable.

The Brookfield viscosity was used to measure the apparent viscosity of the UPR since the standard method of using the Gardner Viscosity has a standard error greater than the variation in the actual viscosity.

[1] The manufacturing of the polyester is discussed in Appendix B.

[2] The specifications listed are for the standard UPR used. The Batches used in this thesis have specifications outside this range to expand the design space.

5.2.3 Design Selection

An empirical statistical model using multiple-linear-regression will be developed (Equation 5.1). The model will be linear with respect to the model parameters (β, γ, and δ) and non-linear with respect to the control (x) and noise (z) factors to allow for non-linear responses and for optimisation.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j}\sum \beta_{ij} x_i x_j + \varepsilon + \sum_{i=1}^{k} \gamma_i z_i + \sum_{i<j}\sum \delta_{ij} x_i z_j \tag{5.1}$$

The preferred approach is to use a RSM combined array model without replication. The experimental data should be regressed to a model as described by equation 5.1 with a high degree of power and low correlation between the model terms. The process can then be optimised using Propagation of Error (PoE).[1]

5.2.3.1 RSM Design Comparison

A design can only truly be evaluated after the experiments have been run, the data compiled and analysed. However this would require excessive effort to run all the alternative design options and then decide which design is most suitable. The design can however be evaluated using the evaluation function of the Design Expert 7® software; which estimates the power at the specified Signal-to-Noise ratio. The desired signal strength (Δy) for the VMD is 2μm; the noise (σ) was calculated as the Standard Deviation of the 5 centre points from the screening experimental design with a value of 1.96μm.

$$\Delta y/_{\sigma} = 2/_{1.96} = 1.02 \tag{5.2}$$

As per the DoE rule of thumb the power should be above 80% for a signal-to-noise ratio of 1.02 (i.e. the chance of making a type II error[2] is less than 20%).

Table 5.3 lists the designs that were evaluated using both the Design-Expert 7® and Statisica® Software[3]. If a DoE had too many experimental runs (>100 i.e. to expensive) or had too low power (<80% for a ratio of 1.02 for main effects (x)) it was deemed not suitable and therefore eliminated.

[1] Described in chapter 3.2.2.

[2] A type II error is accepting that the null hypothesis is true when the alternative hypothesis is correct. I.e. assuming that there is no difference between levels when there is in fact a significant difference.

[3] It is beyond the scope of the project to develop a new design

Table 5.3: Design Comparison.

Type	Design	Design Model	Model Order	Runs	Power (ratio 1.02)[1]			Aliasing
					x	x^2	xy	
Crossed	Taguchi OA	2Lx2L	Linear	32	NA	NA	NA	Complex
Crossed	Taguchi OA	3Lx2L	Linear	72	15.10%	NA	NA	Complex
Crossed	F. Factorial	2Lx2L	Linear	72	33.60%	NA	33.60%	Complex
Fractional Factorial	F. Factorial	Res VI	Res VI	128	99.90%	NA	99.90%	Res IV
RSM	CCD - 1/4	9RSM	Quadratic	156	99.90%	99.30%	99.90%	None
RSM	CCD - Res V	9RSM	Quadratic	70	70.80%	62%	98.50%	None
RSM	BBD	9RSM	Quadratic	125	87.70%	98.70%	38.75%	None
RSM	D-opt	9RSM	Quadratic	65	77%	38%	71.28%	None
RSM	**D-opt +10**	**9RSM**	**Quadratic**	**75**	**86.68%**	**35.31%**	**85.97%**	**None**
RSM	DBD	9RSM	Quadratic	65	34.53%	7.70%	22.70%	None
Fractional Factorial	**3^{9-5} FF**	**9RSM**	**Quadratic**	**81**	**94.00%**	**98.30%**	**57.00%**	**All Interactions**
Fractional Factorial	3^{9-4} FF	9RSM	Quadratic	243	99.90%	99.90%	99.90%	Most Interactions

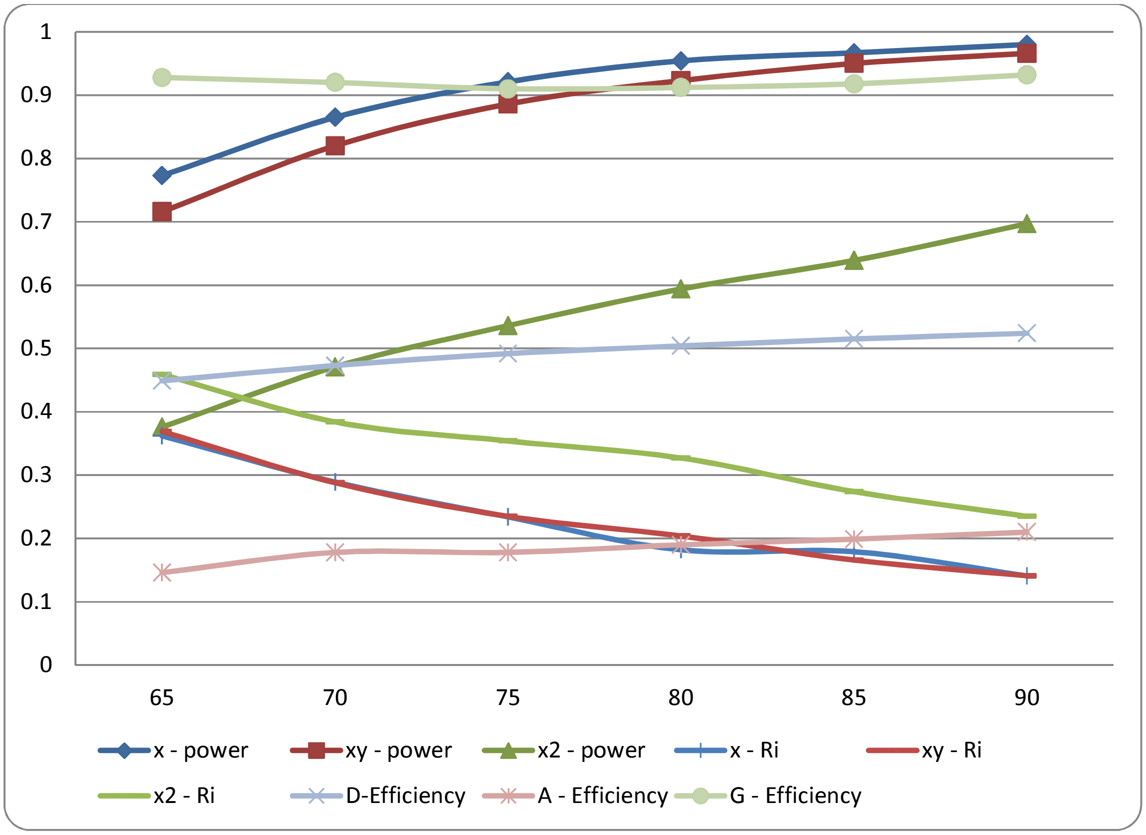
After this elimination 2 DoEs remained: a D-Optimal +10runs and a 3-Level-fractional factorial. The deciding factor between these 2 designs was the power for the interaction and quadratic terms. The D-opt+10 had the superior power for the interaction effects compared to the 3^{9-5}FF and the 3^{9-5}FF had superior power for the quadratic terms. For an RPD problem the interaction effects are of greatest interest and therefore a combined RSM D-Optimal design with additional model points was chosen as the design type.

5.2.3.2 D-Optimal Design Selection

A D-optimal design can have as many design points as the experimenter deems feasible as long as it is above a minimum number, in this case a minimum of 65 design points for 9 factors (55 model points, 5 replicates, & 5 lack-of-fit points). The evaluation criteria power, Ri^2 A-, D- & G-efficiencies, were used to compare D-optimal designs for an increasing number of model design points (65 to 90). The evaluation data is displayed in Figure 5.1.

[1] Please note that the power in this graph is only an average for each factor type and that the actual value for each factor/interaction may differ.

Figure 5.1: Evaluation Criteria for D-Optimal Designs with Increasing Number of Runs.[1]



Whilst 70 experimental runs were sufficient to meet the minimum design criteria (x- & xy-power >80% and x^2-power ~50%) 75 experimental runs were used for the following reasons:

- Minimize risk, if experimental runs fail.
- x & xy – Power >80%
- x^2-Power >50%.
- R_i^2 (measure of co-linearity) is <0.25 for both x and xy terms (x^2 <0.35).
- D-efficiency does not increase significantly with more than 75 runs.

[1] Ri^2: (Average) Ri^2 is a multiple correlation coefficient indicating how much the coefficient for the term is correlated with other terms. A value of zero or as close as possible to zero is preferred.

A-Efficiency: The A-Efficiency is the relative efficiency for the A-optimal criterion of the design. The A-Optimal design tries to minimise the term $\left\{tr\left(X'X\right)^{-1}\right\}$ (Montgomery, 2005). I.e. minimise the sum of the variance of the regression coefficients.

D-Efficiency: The D-Efficiency is the relative efficiency for the D-optimal criterion of the design. The D-Optimal design tries to minimise the term $\left\{\left|\left(X'X\right)^{-1}\right|\right\}$ (Montgomery, 2005). I.e. minimise the confidence interval for the coefficients.

G-Efficiency: The G-Efficiency is the relative efficiency for the G-optimal criterion of the design. The G-Optimal design tries to minimise the term $\left\{\max\left(\frac{NV[\hat{y}(x)]}{\sigma^2}\right)\right\}$ (Montgomery, 2005). I.e. minimise 'the maximum scaled prediction variance over the design region.'

5.2.4 Design Layout

A Combined D-Optimal RSM Design based upon an assumed quadratic response was used to create the design layout for the RPD experimentation. The design consists of 75 design points of which 65 are for the model, 5 are for replicates and 5 points are for estimating the lack of fit of the data.

Unfortunately due to the nature of the UPR variables, the design needs to accommodate the restrictions of the UPR characteristic which has led to a design with the UPR (acid value)^2 & (Viscosity)^2 being aliased with the design's intercept. The final design's evaluation values are listed in Table 5.4.

Table 5.4: Evaluation Criteria for the Chosen Experimental Design.

Design Type	Combined D-Optimal RSM Design
Design Size	75 experiments
Aliasing	Intercept = (acid value)^2 = (Viscosity)^2
Ave Power – x	87.53%
Ave Power – xy	87.65%
Ave Power - x^2 (excl UPR characteristics)	53.6 %
R_i^2 - x	0.24
R_i^2 – xy	0.24
R_i^2 – x^2	0.35
D - Efficiency	51.67%
A - Efficiency	13.74%
G - Efficiency	90.79%

Table 5.5 lists all the experimental factor levels and results for the VMD and Buildup responses. The runs were randomised in accordance with DoE best practice. The procedure and data master record is available as Appendix A.

Table 5.5: RPD DoE used for this Thesis and Results for the VMD and Build-up.[1]

Coded Factor in DX7®		A	B	C	D	E	F	G	H	J		Responses	
Run Number	Std No.	Mass UPR	Mass Styrene	Mass LMA	Mass DETA (Organic)	Mass Water	Stirrer Speed	Initial Reactor Temperature	Acid Value - UPR	Viscosity - UPR	UPR Batch	Buildup	VMD
SCR - 201	71	-13%	0%	0%	0%	0%	350rpm	22.5°C	24.65mgKOH	2273cP	A	0	50.69 µm
SCR - 202	40	0%	-15%	-20%	20%	-6%	300rpm	15°C	24.65mgKOH	2273cP	A	0	35.11 µm
SCR - 203	70	13%	15%	-20%	20%	6%	300rpm	30°C	24.65mgKOH	1880cP	B	0	25.12 µm
SCR - 204	43	-13%	-15%	-20%	20%	0%	400rpm	30°C	24.65mgKOH	1880cP	B	0	45.8 µm
SCR - 205	17	-13%	15%	-20%	20%	-6%	400rpm	30°C	47.84mgKOH	2273cP	D	4	33.4 µm
SCR - 206	51	-13%	15%	-20%	20%	6%	400rpm	15°C	47.84mgKOH	2273cP	D	2	58.88 µm
SCR - 207	66	13%	15%	-20%	-20%	6%	300rpm	15°C	47.84mgKOH	1880cP	C	0	35.08 µm
SCR - 208	60	0%	-15%	20%	-20%	-6%	400rpm	15°C	24.65mgKOH	1880cP	B	1	31.96 µm
SCR - 209	54	13%	15%	20%	20%	-6%	350rpm	15°C	47.84mgKOH	1880cP	C	5	25.1 µm
SCR - 210	15	-13%	15%	-20%	-20%	6%	300rpm	30°C	47.84mgKOH	2273cP	D	0	60.61 µm
SCR - 211	64	-13%	-15%	0%	-20%	-6%	400rpm	30°C	47.84mgKOH	2273cP	D	0	46.89 µm
SCR - 212	74	13%	-15%	-20%	-20%	6%	300rpm	30°C	24.65mgKOH	1880cP	B	0	37.21 µm
SCR - 213	65	-13%	15%	20%	20%	6%	300rpm	30°C	47.84mgKOH	1880cP	C	2	30.73 µm
SCR - 214	49	13%	-15%	-20%	-20%	-6%	300rpm	15°C	47.84mgKOH	2273cP	D	0	67.36 µm
SCR - 215	10	13%	-15%	-20%	20%	6%	300rpm	15°C	47.84mgKOH	2273cP	D	1	77.74 µm
SCR - 216	30	-13%	-15%	20%	20%	-6%	400rpm	22.5°C	47.84mgKOH	1880cP	C	2	22.23 µm
SCR - 217	47	-13%	15%	20%	-20%	0%	400rpm	30°C	47.84mgKOH	1880cP	C	3	23.78 µm
SCR - 218	55	13%	0%	-20%	20%	-6%	300rpm	30°C	47.84mgKOH	1880cP	C	1	26.35 µm
SCR - 219	63	13%	15%	20%	20%	6%	300rpm	30°C	24.65mgKOH	2273cP	A	1	60.4 µm
SCR - 220	34	-13%	15%	-20%	20%	-6%	300rpm	15°C	47.84mgKOH	1880cP	C	3	21.01 µm
SCR - 221	67	13%	15%	-20%	-20%	-6%	300rpm	15°C	24.65mgKOH	1880cP	B	1	21.64 µm
SCR - 222	12	13%	-15%	-20%	-20%	6%	400rpm	15°C	47.84mgKOH	2273cP	D	0	66.18 µm
SCR - 223	24	13%	15%	20%	-20%	0%	300rpm	30°C	24.65mgKOH	1880cP	B	1	31.12 µm
SCR - 224	5	-13%	15%	-20%	20%	6%	300rpm	30°C	24.65mgKOH	2273cP	A	0	64.64 µm
SCR - 225	61	-13%	-15%	-20%	20%	0%	300rpm	30°C	47.84mgKOH	2273cP	D	0	72.09 µm
SCR - 226	8	-13%	15%	-20%	-20%	6%	400rpm	30°C	24.65mgKOH	2273cP	A	0	28.14 µm
SCR - 227	42	-13%	15%	-20%	-20%	-6%	300rpm	30°C	24.65mgKOH	2273cP	A	1	31.38 µm

[1] Refer to Table E.1 for the uncoded values & Table E.2 for all the responses' results.

Coded Factor in DX7®		A	B	C	D	E	F	G	H	J		Responses	
Run Number	**Std No.**	**Mass UPR**	**Mass Styrene**	**Mass LMA**	**Mass DETA (Organic)**	**Mass Water**	**Stirrer Speed**	**Initial Reactor Temperature**	**Acid Value - UPR**	**Viscosity - UPR**	**UPR Batch**	**Buildup**	**VMD**
SCR - 228	4	13%	15%	20%	20%	-6%	300rpm	15°C	24.65mgKOH	2273cP	A	1	43.77 µm
SCR - 229	28	13%	-15%	0%	-20%	-6%	300rpm	30°C	24.65mgKOH	2273cP	A	0	45.4 µm
SCR - 230	29	-13%	0%	20%	-20%	6%	300rpm	15°C	47.84mgKOH	1880cP	C	0	44.03 µm
SCR - 231	9	-13%	15%	20%	20%	-6%	300rpm	15°C	47.84mgKOH	2273cP	D	3	52.22 µm
SCR - 232	45	-13%	-15%	20%	20%	-6%	300rpm	15°C	24.65mgKOH	2273cP	A	5	44.27 µm
SCR - 233	21	13%	15%	20%	-20%	6%	400rpm	15°C	47.84mgKOH	2273cP	D	0	61.07 µm
SCR - 234	33	13%	15%	-20%	20%	6%	400rpm	22.5°C	47.84mgKOH	1880cP	C	5	20.34 µm
SCR - 235	25	13%	15%	20%	-20%	-6%	300rpm	22.5°C	47.84mgKOH	1880cP	C	1	32.99 µm
SCR - 236	72	-13%	15%	20%	20%	-6%	300rpm	15°C	47.84mgKOH	2273cP	D	2	63.64 µm
SCR - 237	39	0%	15%	-20%	-20%	-6%	400rpm	15°C	47.84mgKOH	1880cP	C	2	19.58 µm
SCR - 238	31	13%	-15%	-20%	-20%	6%	300rpm	30°C	47.84mgKOH	1880cP	C	0	49.61 µm
SCR - 239	68	-13%	15%	20%	-20%	-6%	300rpm	15°C	24.65mgKOH	1880cP	B	1	42.55 µm
SCR - 240	73	-13%	15%	-20%	20%	-6%	300rpm	15°C	47.84mgKOH	1880cP	C	3	24.13 µm
SCR - 241	20	13%	15%	20%	20%	6%	400rpm	30°C	24.65mgKOH	1880cP	B	4	20.76 µm
SCR - 242	2	-13%	15%	20%	20%	6%	400rpm	15°C	24.65mgKOH	1880cP	B	2	51.8 µm
SCR - 243	38	13%	-15%	20%	-20%	6%	350rpm	15°C	24.65mgKOH	2273cP	A	1	58.57 µm
SCR - 244	7	-13%	-15%	20%	20%	-6%	400rpm	30°C	24.65mgKOH	2273cP	A	0	39.25 µm
SCR - 245	35	13%	15%	-20%	20%	0%	400rpm	15°C	24.65mgKOH	2273cP	A	0	21.3 µm
SCR - 246	23	13%	15%	0%	-20%	6%	400rpm	15°C	24.65mgKOH	1880cP	B	3	21.56 µm
SCR - 247	27	-13%	0%	0%	0%	0%	350rpm	22.5°C	24.65mgKOH	2273cP	A	0	48.17 µm
SCR - 248	6	-13%	15%	20%	-20%	-6%	400rpm	30°C	24.65mgKOH	2273cP	A	2	35.27 µm
SCR - 249	41	-13%	-15%	20%	-20%	6%	400rpm	30°C	24.65mgKOH	1880cP	B	0	48.79 µm
SCR - 250	44	13%	-15%	-20%	0%	-6%	400rpm	30°C	47.84mgKOH	1880cP	C	2	26.52 µm
SCR - 251	18	13%	-15%	-20%	20%	6%	400rpm	30°C	47.84mgKOH	2273cP	D	0	48.55 µm
SCR - 252	16	13%	15%	-20%	-20%	-6%	400rpm	30°C	47.84mgKOH	2273cP	D	4	29.69 µm
SCR - 253	59	13%	-15%	-20%	20%	6%	350rpm	15°C	24.65mgKOH	1880cP	B	1	17.06 µm
SCR - 254	36	13%	-15%	-20%	-20%	-6%	400rpm	22.5°C	24.65mgKOH	1880cP	B	0	19.16 µm
SCR - 255	46	13%	15%	20%	20%	-6%	400rpm	30°C	47.84mgKOH	2273cP	D	4	36.4 µm
SCR - 256	69	-13%	-15%	-20%	-20%	6%	400rpm	15°C	24.65mgKOH	1880cP	B	1	35.48 µm
SCR - 257	19	-13%	-15%	20%	20%	6%	400rpm	30°C	47.84mgKOH	2273cP	D	0	71 µm
SCR - 258	37	-13%	-15%	-20%	20%	6%	350rpm	15°C	47.84mgKOH	1880cP	C	0	33.32 µm
SCR - 259	13	-13%	-15%	20%	-20%	6%	400rpm	15°C	47.84mgKOH	2273cP	D	0	56.13 µm

Coded Factor in DX7®		A	B	C	D	E	F	G	H	J		Responses	
Run Number	Std No.	Mass UPR	Mass Styrene	Mass LMA	Mass DETA (Organic)	Mass Water	Stirrer Speed	Initial Reactor Temperature	Acid Value - UPR	Viscosity - UPR	UPR Batch	Buildup	VMD
SCR - 260	53	-13%	-15%	20%	-20%	-6%	300rpm	30°C	47.84mgKOH	1880cP	C	0	49.4 µm
SCR - 261	14	13%	-15%	20%	20%	-6%	300rpm	30°C	47.84mgKOH	2273cP	D	0	79.27 µm
SCR - 262	75	-13%	-15%	20%	20%	-6%	400rpm	22.5°C	47.84mgKOH	1880cP	C	2	25.22 µm
SCR - 263	58	13%	-15%	-20%	0%	6%	300rpm	30°C	24.65mgKOH	2273cP	A	0	45.6 µm
SCR - 264	32	-13%	0%	-20%	-20%	6%	300rpm	15°C	24.65mgKOH	2273cP	A	1	58.6 µm
SCR - 265	26	13%	15%	20%	-20%	-6%	300rpm	15°C	24.65mgKOH	2273cP	A	1	39.77 µm
SCR - 266	57	13%	-15%	20%	0%	6%	400rpm	15°C	47.84mgKOH	1880cP	C	0	46.62 µm
SCR - 267	22	0%	15%	20%	20%	6%	300rpm	15°C	24.65mgKOH	1880cP	B	5	54.91 µm
SCR - 268	52	-13%	15%	0%	20%	-6%	400rpm	30°C	24.65mgKOH	1880cP	B	5	34.05 µm
SCR - 269	56	-13%	-15%	0%	20%	6%	400rpm	15°C	24.65mgKOH	2273cP	A	4	34.08 µm
SCR - 270	1	-13%	-15%	-20%	-20%	-6%	300rpm	15°C	24.65mgKOH	1880cP	B	1	34.13 µm
SCR - 271	50	-13%	15%	-20%	-20%	-6%	350rpm	15°C	24.65mgKOH	2273cP	A	1	35.26 µm
SCR - 272	62	13%	0%	20%	-20%	6%	300rpm	30°C	47.84mgKOH	2273cP	D	0	70.46 µm
SCR - 273	3	13%	-15%	20%	20%	6%	300rpm	30°C	24.65mgKOH	1880cP	B	0	54.67 µm
SCR - 274	11	13%	-15%	-20%	20%	-6%	400rpm	15°C	47.84mgKOH	2273cP	D	0	48.3 µm
SCR - 275	48	-13%	15%	-20%	0%	6%	300rpm	30°C	47.84mgKOH	1880cP	C	1	31.05 µm

5.3 Volume Mean Diameter (VMD) Model Analysis

5.3.1 VMD Model Development

Table 5.6: Model Summary Statistics for the VMD Response.

Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	9.80	0.67	0.62	0.56	
2FI	**5.12**	**0.96**	**0.90**	**0.63**	**Suggested**
Quadratic	5.40	0.97	0.89	0.45	Aliased
Cubic	4.41	1.00	0.92	-	Aliased

The Design Expert 7® model summary indicated that 2FI model best fitted the data with insignificant lack of fit (p-value = 0.4093). The high R^2 value indicated that the model fitted the data well but the low Predicted R^2 value suggests that the model needed to be refined to accurately predict the VMD.

Backward selection[1] of the terms from an initial 2FI model was used to reduce the model to only the terms which are significant at the $\alpha = 0.1$ level. The factors, Mass DETA in the Organic Phase (D) & Initial Reactor Temperature (G), were found to not be significant but were retained to maintain model hierarchy. 18 of the initial 45 terms were removed by the backward selection.

[1] Backward selection was used over forward or step-wise selection due to the collinearity within the design indicated by the non-zero values of R_i^2 (Section 5.2.3.2). When forward or step-wise selection is used they risk ignoring model terms if the selection criteria of $\alpha = 0.1$ is met before the term has been considered in the selection process.
See Appendix E.5 for the model comparison of the 3 selection methods.

Table 5.7: ANOVA Results for VMD.[1]

Removed Terms:

AF, AJ, BC, BE, BF, BJ, CD, CE, CF, CG, CJ, DE, DF, EF, EH, FG, FH & GJ

Hierarchical Terms:

D - Mass DETA (Organic); G - Initial Temperature

Source	Sum of Squares	df	Mean SS	F-Value	p-value[2]
Model	17648.25	27	653.64	27.29	**< 0.0001**
A-Mass UPR	436.77	1	436.77	18.23	**< 0.0001**
B-Mass Styrene	1200.73	1	1200.73	50.12	**< 0.0001**
C-Mass LMA	1339.61	1	1339.61	55.92	**< 0.0001**
D-Mass DETA (Organic)	0.14	1	0.14	0.01	0.9399
E-Mass Water	1696.74	1	1696.74	70.83	**< 0.0001**
F-Stirrer Speed	2522.78	1	2522.78	105.31	**< 0.0001**
G-Initial Reactor Temp.	0.09	1	0.09	0.00	0.9512
H-Acid Value	808.82	1	808.82	33.76	**< 0.0001**
J-Viscosity	4350.87	1	4350.87	181.62	**< 0.0001**
AB	230.28	1	230.28	9.61	**0.0033**
AC	145.91	1	145.91	6.09	**0.0173**
AD	17.27	1	17.27	0.72	0.4002
AE	68.26	1	68.26	2.85	0.0980
AG	161.35	1	161.35	6.74	**0.0126**
AH	804.12	1	804.12	33.57	**< 0.0001**
BD	184.59	1	184.59	7.71	**0.0079**
BG	612.40	1	612.40	25.56	**< 0.0001**
BH	281.06	1	281.06	11.73	**0.0013**
CH	156.65	1	156.65	6.54	**0.0138**
DG	85.39	1	85.39	3.56	0.0652
DH	108.50	1	108.50	4.53	**0.0386**
DJ	92.84	1	92.84	3.88	0.0549
EG	81.87	1	81.87	3.42	0.0708
EJ	118.23	1	118.23	4.94	**0.0312**
FJ	245.49	1	245.49	10.25	**0.0025**
GH	94.56	1	94.56	3.95	0.0528
HJ	1719.55	1	1719.55	71.78	**< 0.0001**
Residual	1125.92	47	23.96		
Lack of Fit	1048.20	43	24.38	1.25	0.4663
Pure Error	77.72	4	19.43		
Cor Total	18774.16	74			

[1] For a full explanation of each term refer to Appendix D.

[2] Significant Values (95% level) in **Bold**.

Table 5.7: ANOVA Results for VMD. (Ctd)

Root MSE	4.89
Mean	41.79
C.V. %	11.71
PRESS	3013.82

R^2	0.940
Adj R^2	0.906
Pred R^2	0.839
Adeq Precision	20.55

Factor	**Coefficient Estimate**	**Df**	**Standard Error**	**95% CI - Low**	**95% CI - High**
Intercept	41.68	1	0.58	40.51	42.85
A-Mass UPR	-2.61	1	0.61	-3.84	-1.38
B-Mass Styrene	-4.57	1	0.65	-5.87	-3.27
C-Mass LMA	4.74	1	0.63	3.47	6.02
D-Mass DETA (Organic)	-0.05	1	0.62	-1.29	1.20
E-Mass Water	5.39	1	0.64	4.11	6.68
F-Stirrer Speed	-7.21	1	0.70	-8.63	-5.80
G-Initial Reactor Temp.	-0.04	1	0.61	-1.26	1.19
H-Acid Value	3.50	1	0.60	2.29	4.71
J-Viscosity	8.03	1	0.60	6.83	9.23
AB	-2.15	1	0.69	-3.54	-0.75
AC	1.73	1	0.70	0.32	3.13
AD	-0.55	1	0.65	-1.86	0.76
AE	-1.09	1	0.64	-2.38	0.21
AG	-1.71	1	0.66	-3.03	-0.38
AH	3.70	1	0.64	2.42	4.99
BD	1.79	1	0.64	0.49	3.08
BG	-3.30	1	0.65	-4.61	-1.99
BH	-2.17	1	0.63	-3.44	-0.90
CH	-1.59	1	0.62	-2.84	-0.34
DG	1.24	1	0.65	-0.08	2.55
DH	-1.37	1	0.65	-2.67	-0.08
DJ	1.25	1	0.64	-0.03	2.53
EG	-1.29	1	0.70	-2.70	0.11
EJ	1.41	1	0.63	0.13	2.69
FJ	-2.03	1	0.64	-3.31	-0.76
GH	-1.24	1	0.63	-2.50	0.02
HJ	5.15	1	0.61	3.93	6.37

The ANOVA indicated that the regressed model is significant (p-value <0.0001) with the following significant terms (α= 0.1 Level): A, B, C, E, F, H, J, AB, AC, AD, AE, AG, AH, BD, BG, BH, CH, DG, DH, DJ, EG, EJ, FJ, GH & HJ. It should be noted that of the interaction terms 9 out of the 18 are interactions with the UPR characteristics.

The model fits the data well as indicated by the high R^2 value of 0.940 and the non-significant lack of fit. The Pred R^2 value of 0.839 indicates that the model should predict all future values of the VMD with a high degree of accuracy.

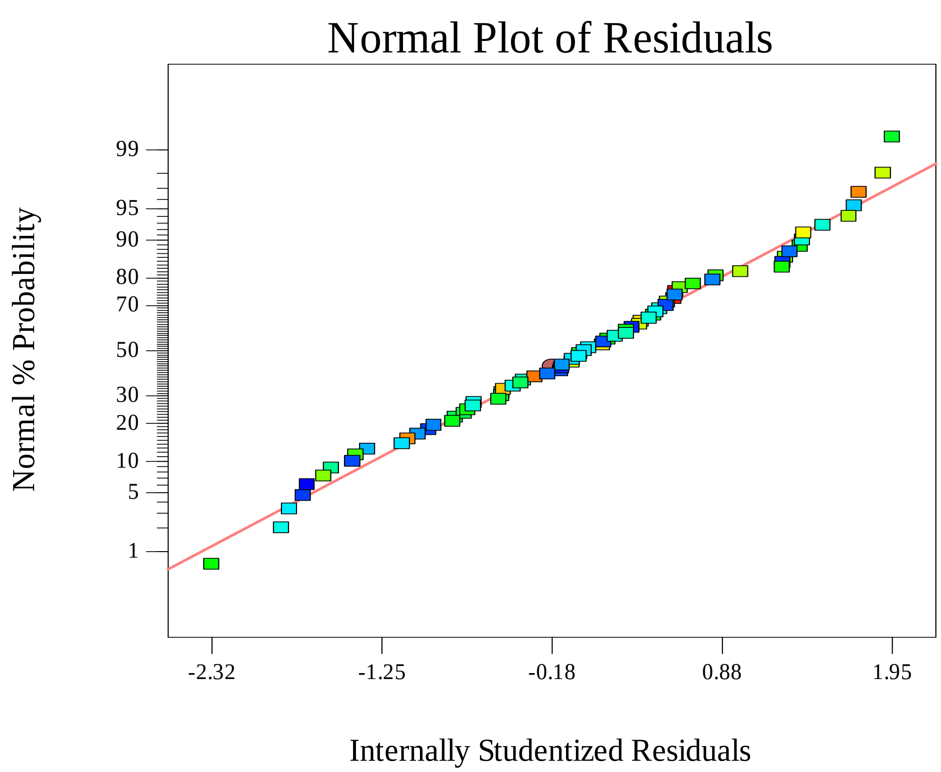
The fitted model[1] for the Volume-Mean-Diameter Response is as follows:

$$\begin{aligned} VMD = {} & 41.68 - 2.61A - 4.57B + 4.74C - 0.05D + 5.39E - 7.21F - 0.04G + 3.50H \\ & +8.03J - 2.15AB + 1.73AC - 0.55AD - 1.09AE - 1.71AG + 3.70AH + 1.79BD \\ & -3.30BG - 2.17BH - 1.59CH + 1.24DG - 1.37DH + 1.25DJ - 1.29EG + 1.41EJ \\ & -2.03FJ - 1.24GH + 5.15HJ \end{aligned} \tag{5.3}$$

5.3.2 VMD Model Diagnostics

The following diagnostics are for the VMD model equation 5.3; the diagnostic methods were discussed in Chapter 3 – Table 3.1.

Figure 5.2: Normal Plot of Residuals for the VMD Response.



[1] The model is in coded units (-1 to 1) for comparison of the modelled terms.

Figure 5.3: Residuals vs. Predicted Response for the VMD Response.

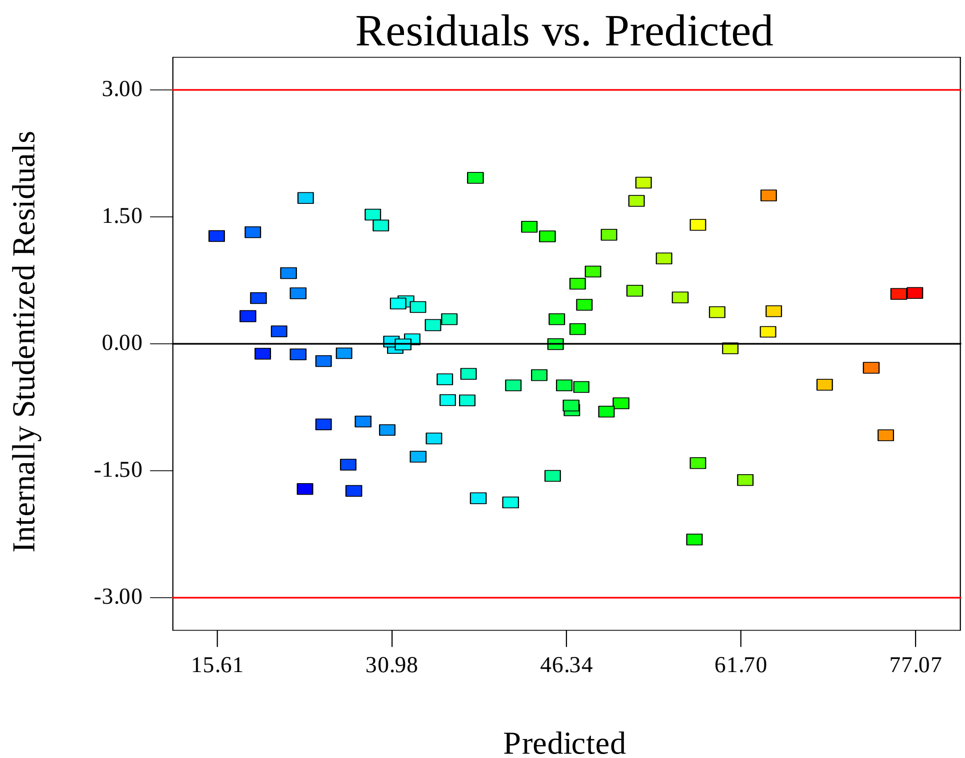


Figure 5.4: Residuals vs. Run Order for the VMD Response.

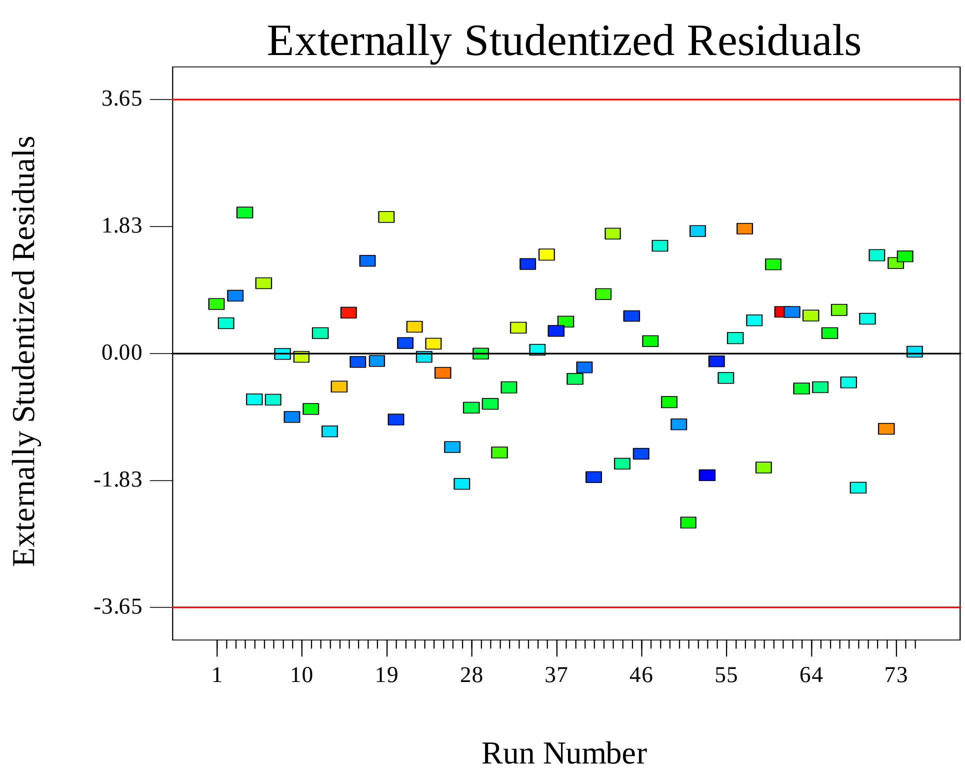


Figure 5.5: Cook's Distance for the VMD Response.

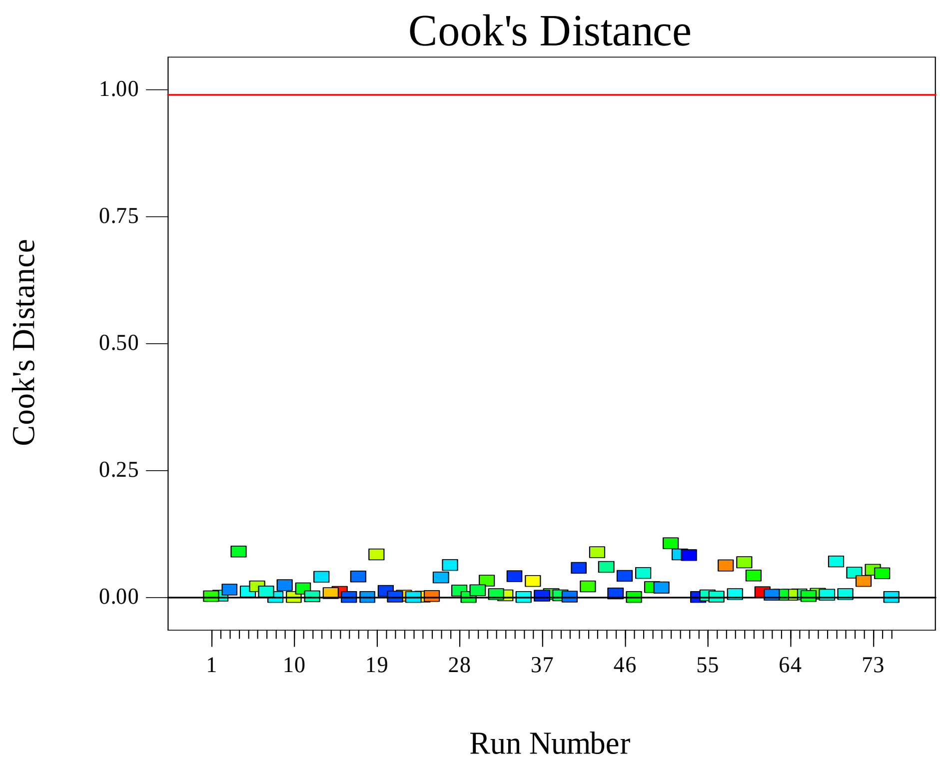
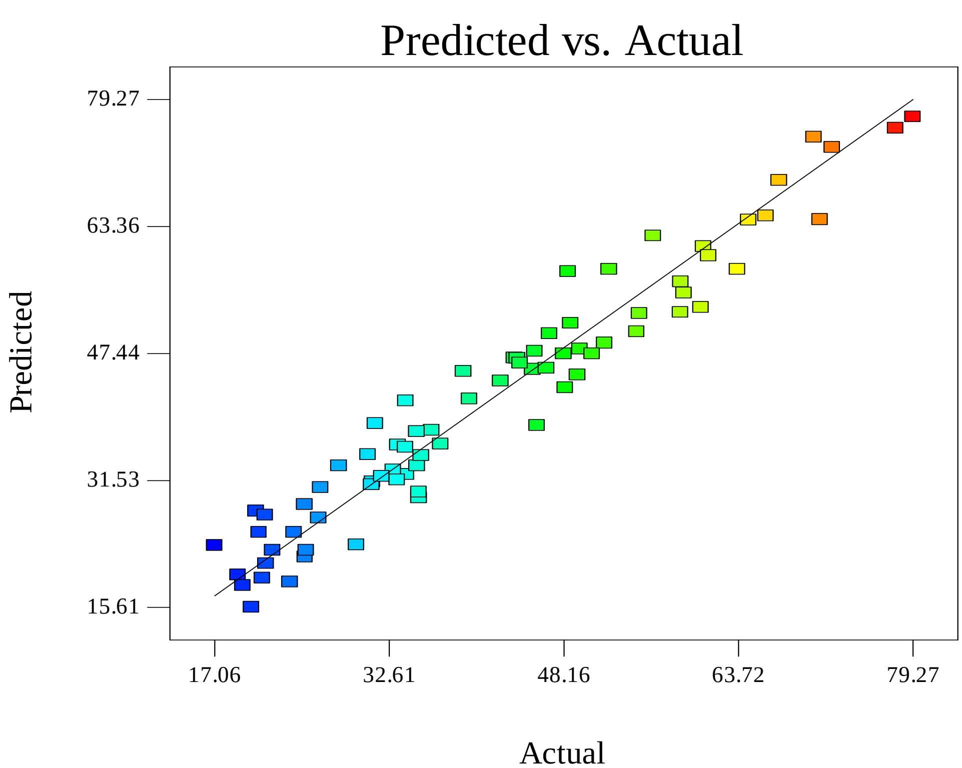


Figure 5.6: Predicted vs. Actual Response Plot for the VMD Response.



The assumption of normality is validated by Figure 5.2; the lack of observable trends in either Figure 5.3 or Figure 5.4 indicates that the assumptions of sample independence and homoscedasticity are valid. None of the samples lie outside of the t-limits and none of the samples have excessive leverage over the model which suggests that there were no outliers in the data set.

The samples fall along the 45° line in Figure 5.6 with minimal variation. This visually indicates that the model should have a high degree of predictability as indicated from the Pred-R^2 value of 0.839.

5.4 Buildup Model Analysis

5.4.1 Buildup Model Development

After an initial analysis of the response it was determined that to obtain the best fit model that a logarithmic transformation will be used such that for the model:

$$y' = \ln(Buildup + 0.05) \tag{5.4}$$

Table 5.8: Model Summary Statistics for the Buildup Response.

Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	1.47	0.46	0.39	0.28	
2FI	**1.05**	**0.88**	**0.69**	**0.20**	**Suggested**
Quadratic	1.02	0.91	0.71	-0.32	Aliased
Cubic	0.14	1.00	0.99	-	Aliased

The DX7® model summary indicated that 2FI model best fitted the data with the drawback of significant lack-of-fit (p-value = 0.0005). The R^2 value indicated that the model represents the data sufficiently but the low Predicted R^2 value suggests that the model needs significant refinement to accurately predict the Buildup.

Backward selection[1] of the terms from an initial 2FI model was used to reduce the model to only the terms which are significant at the α = 0.1 level. The factors, Mass UPR (A), Stirrer Speed (F) & UPR Acid Value (H), were found not to be significant but were retained to maintain model hierarchy. 22 of the initial 45 terms were removed by the backward selection.

[1] Backward selection was used over forward or step-wise selection due to the collinearity within the design indicated by the non-zero values of R_i^2 (Section 5.2.3.2). When forward or step-wise selection is used they risk ignoring model terms if the selection criteria of α = 0.1 is met before the term has been considered in the selection process.
See Appendix E.5 for the model comparison of the 3 selection methods.

Table 5.9: ANOVA Results for Buildup.[1]

Removed Terms:

AB, AC, AD, AF, AG, AH, AJ, BC, BD, BF, BJ, CE, CF, CG, CJ, DF, DG, DJ, EF, FG, FH & HJ

Hierarchical Terms:

A - Mass Polyester; F - Stirrer Speed; H - Acid Value

Source	Sum of Squares	Df	Mean SS	F-Value	p-value[2]
Model	219.19	23	9.53	11.09	**< 0.0001**
A-Mass UPR	0.63	1	0.63	0.73	0.3962
B-Mass Styrene	63.98	1	63.98	74.46	**< 0.0001**
C-Mass LMA	5.39	1	5.39	6.27	**0.0155**
D-Mass DETA (Organic)	9.02	1	9.02	10.50	**0.0021**
E-Mass Water	7.72	1	7.72	8.98	**0.0042**
F-Stirrer Speed	0.52	1	0.52	0.61	0.4382
G-Initial Reactor Temp.	6.75	1	6.75	7.85	**0.0072**
H-Acid Value	0.02	1	0.02	0.02	0.8807
J-Viscosity	12.29	1	12.29	14.30	**0.0004**
AE	7.16	1	7.16	8.33	**0.0057**
BE	5.80	1	5.80	6.75	**0.0122**
BG	15.89	1	15.89	18.49	**< 0.0001**
BH	8.43	1	8.43	9.81	**0.0029**
CD	11.16	1	11.16	12.99	**0.0007**
CH	11.52	1	11.52	13.40	**0.0006**
DE	4.89	1	4.89	5.69	**0.0209**
DH	13.42	1	13.42	15.62	**0.0002**
EG	10.11	1	10.11	11.76	**0.0012**
EH	6.06	1	6.06	7.05	**0.0105**
EJ	5.58	1	5.58	6.50	**0.0139**
FJ	6.23	1	6.23	7.25	**0.0096**
GH	19.60	1	19.60	22.81	**< 0.0001**
GJ	6.50	1	6.50	7.56	**0.0082**
Residual	43.82	51	0.86		
Lack of Fit	43.74	47	0.93	47.17	**0.0009**
Pure Error	0.08	4	0.02		
Cor Total	263.01	74			

Root MSE	0.93
Mean	-0.94
C.V. %	98.12
PRESS	91.05

R^2	0.833
Adj R^2	0.758
Pred R^2	0.654
Adeq Precision	11.60

[1] For a full explanation of each term refer to Appendix D.

[2] Significant Values (95% level) in **Bold.**

Table 5.9: ANOVA Results for Buildup. (Ctd)

Factor	Coefficient Estimate	Df	Standard Error	95% CI - Low	95% CI - High
Intercept	-1.07	1	0.11	-1.29	-0.85
A-Mass UPR	-0.10	1	0.11	-0.33	0.13
B-Mass Styrene	1.01	1	0.12	0.77	1.24
C-Mass LMA	0.29	1	0.12	0.06	0.53
D-Mass DETA (Organic)	0.39	1	0.12	0.15	0.62
E-Mass Water	-0.36	1	0.12	-0.60	-0.12
F-Stirrer Speed	0.10	1	0.12	-0.15	0.34
G-Initial Reactor Temp.	-0.33	1	0.12	-0.56	-0.09
H-Acid Value	0.02	1	0.12	-0.21	0.25
J-Viscosity	-0.42	1	0.11	-0.65	-0.20
AE	0.35	1	0.12	0.11	0.60
BE	-0.32	1	0.12	-0.57	-0.07
BG	0.52	1	0.12	0.28	0.77
BH	0.36	1	0.12	0.13	0.60
CD	0.45	1	0.12	0.20	0.70
CH	-0.43	1	0.12	-0.67	-0.19
DE	0.30	1	0.13	0.05	0.56
DH	0.48	1	0.12	0.23	0.72
EG	-0.46	1	0.13	-0.72	-0.19
EH	-0.32	1	0.12	-0.56	-0.08
EJ	0.30	1	0.12	0.06	0.54
FJ	-0.32	1	0.12	-0.56	-0.08
GH	0.56	1	0.12	0.32	0.79
GJ	-0.33	1	0.12	-0.57	-0.09

The ANOVA indicated that the regressed model is significant (p-value <0.0001) with the following significant terms (α= 0.1 level): B, C, D, E, G, J, AE, BE, BG, BH, CD, CH, DE, DH, EG, EH, EJ, FJ, GH & GJ. It should be noted that of the interaction terms 8 out of the 14 are interactions with the UPR's characteristics.

The model fits the data reasonably well as indicated by the R^2 value of 0.833.The significant lack of fit is of concern and therefore in conjunction with the average Pred-R^2 value of 0.654 the accuracy of the predicted variables is questionable.

The fitted model[1] for the Buildup Response is as follows:

$$\begin{aligned}\ln(Buildup + 0.05) = {} & -1.070 - 0.098A + 1.008B + 0.292C - 0.386D - 0.357E + 0.095F \\ & -0.327G + 0.017H - 0.422J + 0.352AE - 0.319BE + 0.522BG + 0.365BH \\ & +0.450CD - 0.430CH + 0.305DE + 0.477DH - 0.456EG - 0.322EH \\ & +0.305EJ - 0.322FJ + 0.557GH - 0.329GJ \qquad (5.5)\end{aligned}$$

[1] The model is in coded units (-1 to 1) for comparison of the modelled terms.

5.4.2 Buildup Model Diagnostics

The following diagnostics are for the Buildup model equation 5.5; the diagnostic methods were discussed in Chapter 3 – Table 3.1.

Figure 5.7: Normal Plot of Residuals for the ln(Buildup+0.05) Response.

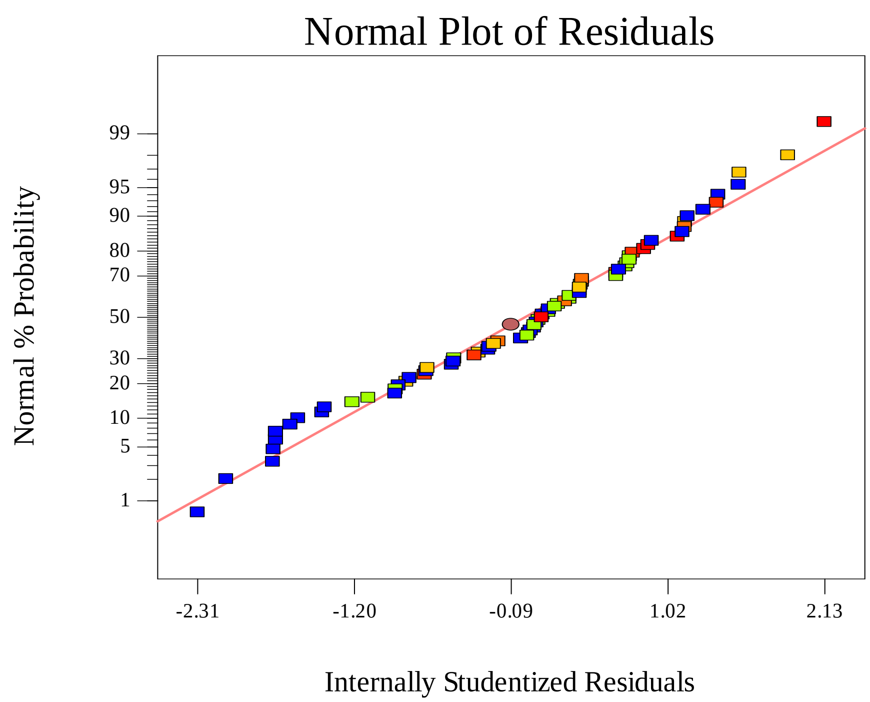


Figure 5.8: Residuals vs. Predicted Response for the ln(Buildup+0.05) Response.

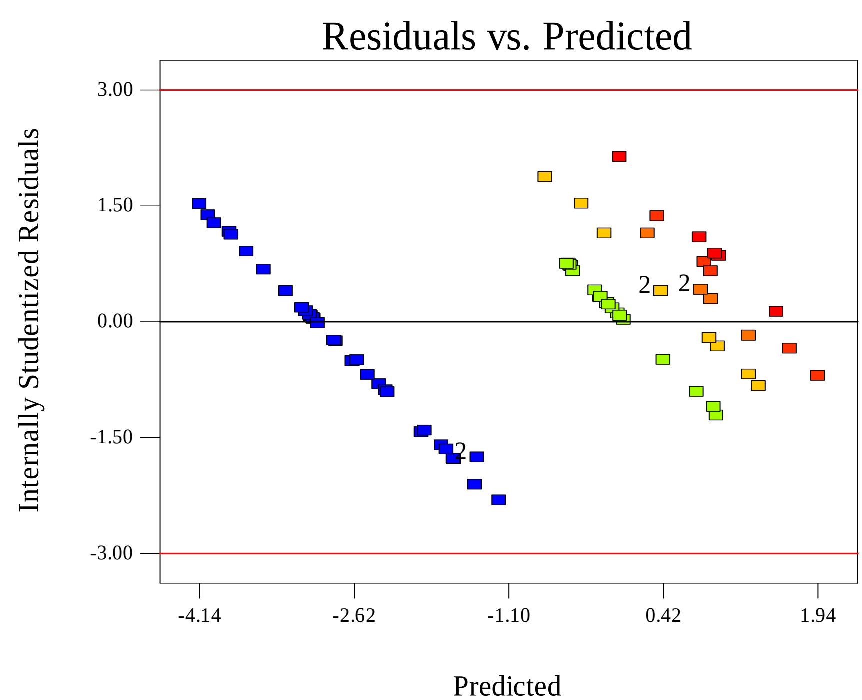


Figure 5.9: Residuals vs. Run Order for the ln(Buildup+0.05) Response.

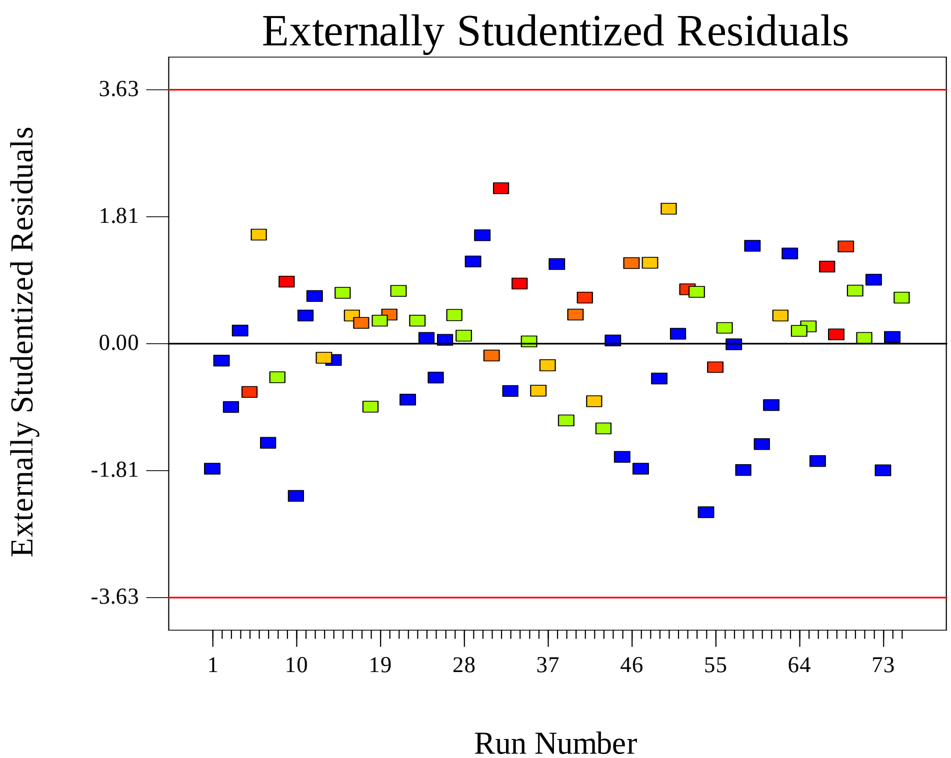


Figure 5.10: Cook's Distance for the ln(Buildup+0.05) Response.

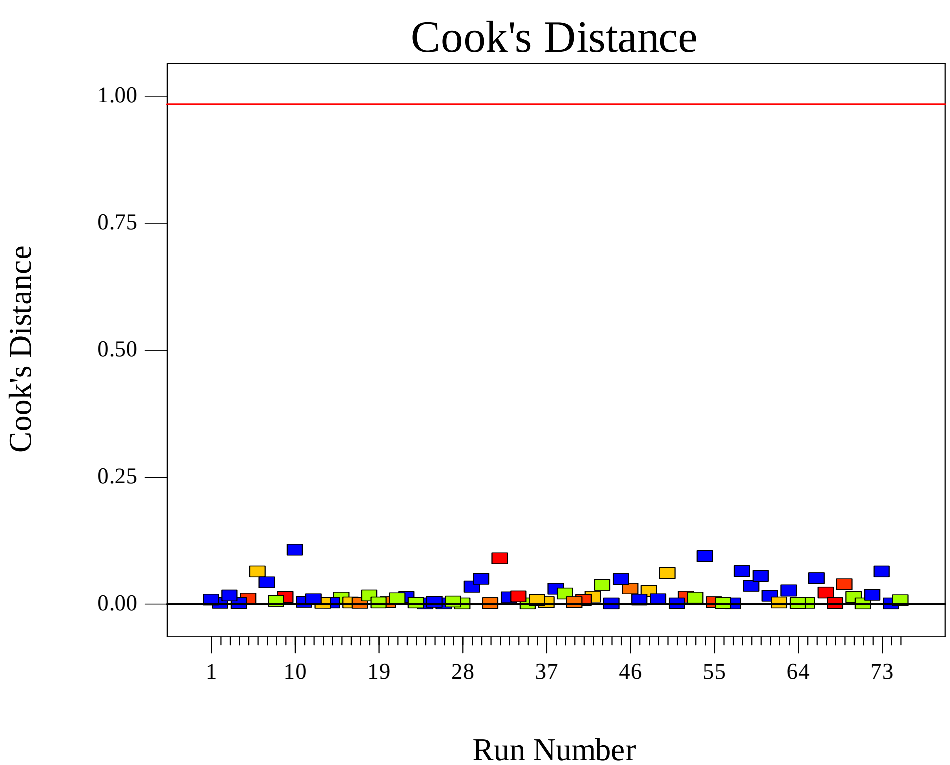
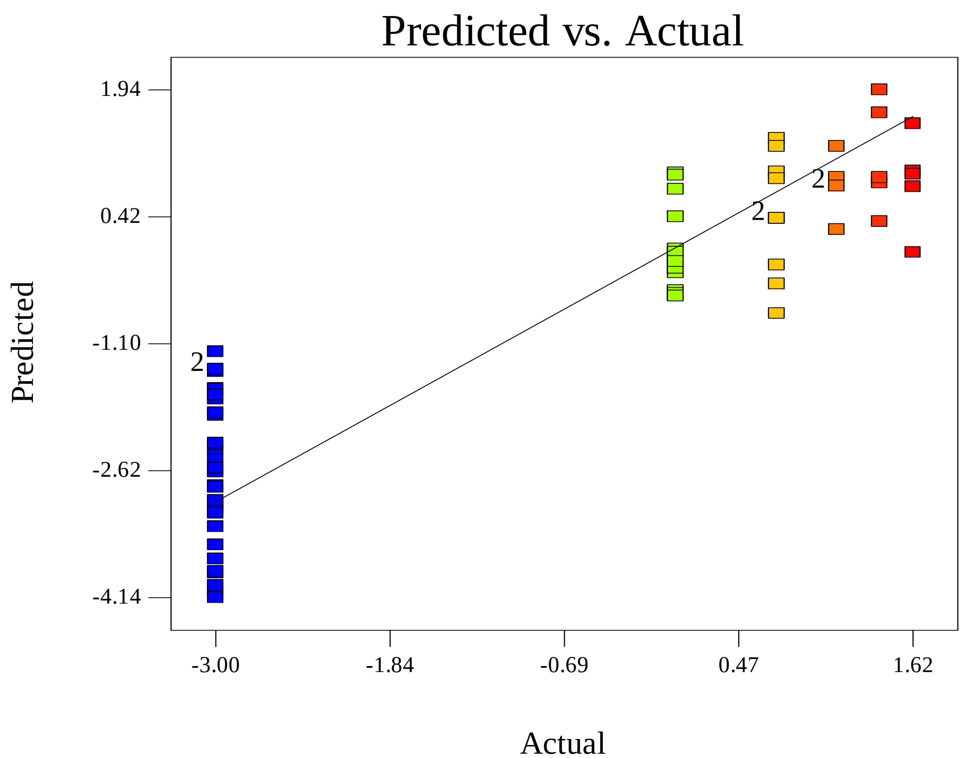


Figure 5.11: Predicted vs. Actual Response Plot for the ln(Buildup+0.05) Response.



The assumption of normality is validated by Figure 5.7; the lack of observable trends in Figure 5.9 indicates that the assumptions of sample independence and homoscedasticity are valid. None of the samples lie outside of the t-limits and none of the samples have excessive leverage over the model which suggests that there were no outliers in the data set.

The predictability of the model is poor as observed in Figure 5.11. This is most likely due to the discrete interval nature of the Buildup response and therefore the model cannot be relied upon for accurate predictions.

5.5 Model Interpretation

5.5.1 Interpretation of the VMD Model

The VMD model selection and statistical validation has already been discussed in Chapter 5.3. From the ANOVA results for the VMD (Table 5.7) the following interpretation of the model can be made:

The model is clearly significant with only a 0.01% chance that this result was due to noise. The insignificant lack-of-fit for the model as well as the considerably high R^2 value (0.940) are good indications that the model fits the experimental data well. The predicted variation of the response data (Pred R^2 = 0.839) explained by the model is sufficiently high for reasonably accurate prediction of the VMD for experimental data.

Equation Comparison:

$$\begin{aligned} VMD = {} & 41.68 - 2.61A - 4.57B + 4.74C - 0.05D + 5.39E - 7.21F - 0.04G + 3.50H \\ & +8.03J - 2.15AB + 1.73AC - 0.55AD - 1.09AE - 1.71AG + 3.70AH + 1.79BD \\ & -3.30BG - 2.17BH - 1.59CH + 1.24DG - 1.37DH + 1.25DJ - 1.29EG + 1.41EJ \\ & -2.03FJ - 1.24GH + 5.15HJ \end{aligned} \quad (5.3)$$

$$VMD = 41.62 - 8.33A - 4.99B + 6.51C - 0.25D + 8.06E - 4.73F - 3.57AD \quad (4.2)^{1}$$

When comparing the two models it was interesting to note that the intercept (overall mean) and mass styrene (B) coefficient were similar in value. The other main effect coefficients differed considerably but this is most likely due to the difference in the order of the model. The models are in agreement for the trend of all the main effect coefficients regardless if the magnitudes of the coefficients differ.

The mass of DETA added to the organic phase (D) and the initial reactor temperature (G) were found to not be statistically significant in both designs. The trend of the DETA having a decreasing influence on the VMD was observed in both models.

It is worth noting that the 2-factor interaction, AD (Mass Polyester × Mass DETA), of the screening model (equation 4.2) was confounded with the EG (Mass Water × Initial Temperature) interaction. Both are significant and appear in the RPD model (equation 5.3) this suggests that the initial interpretation of the significance of this term in the screening phase of this thesis was correct but did not cover all the information. This highlights the difficulties with confounding in screening designs and the information which can be lost in the aliasing structure.

Main Effect Interpretation:

An increase in the mass of UPR (A) added to the formulation was found to have an overall decreasing effect on the VMD. This is as expected since the resulting increase in hold-up, should increase the rate of breakage and reduce the coalescent rate of the dispersed phase droplets. The mass of UPR had interaction effects with all the model factors with the exception of the UPR's viscosity factor (J).

[1] Variable references have been changed to be directly comparable to equation 5.3.

An increase in the mass of styrene (B) added to the formulation, was found to have an overall decreasing effect on the VMD. This is as expected since the resulting increase in hold-up, and decrease in both the viscosity & density of the dispersed phase should increase the rate of breakage and reduce the coalescent rate of the dispersed phase droplets (*Polymerization Processes*, 1992). The factor B only has interactions with the mass of polyester (A), mass DETA (D), Initial reactor temperature (G) and the UPR acid value (H).

As mentioned previously an increasing quantity of LMA (C) has been confirmed to increase the VMD, this was confirmed by the RPD model results. The RPD model indicated that the Mass LMA (C) has a slightly lesser effect on the VMD than the screening model did; however the difference in the influence of factor C is most likely incorporated in the interaction effects.

An increase in the quantity of water (E) added is known to increase the VMD as observed in the work by Terblanche (2002) (see Chapter 4.5.2 for a full discussion). The addition of the water to the aqueous phase has an overall effect of reducing the viscosity of the aqueous phase, hence reducing the ${}^{\mu_d}/_{\mu_c}$ ratio, and according to *Polymerization Processes* (1992) an increasing effect on the VMD.

The stirrer speed (F) is known to affect the VMD of a suspension polymerisation as is reported in literature (Yuan et. al., 1991; *Polymerization Processes,* 1992)) and in the previous work on the MVP by Terblanche (2002). The increase in factor F is known to have a decreasing effect on the VMD as was observed by the screening model and the RPD model.

The other two main effects, mass DETA (D) & the initial reactor temperature (G) were found not to be statistically significant in their own right and were only retained in the model to maintain the model's hierarchy.

2-Factor Interactions Interpretation:

It is difficult to clearly interpret 2-factor and higher order interactions of a model directly, particularly when each of the terms in the interaction participate in multiple interaction effects. However, if statistically significant correlations (Appendix E.3) can be found between interaction effects and the system's parameters, it is not unreasonable to interpret the correlations as the effect (but not cause) of the interaction terms.

The negative interaction between the mass of UPR (A) & Styrene (B) is of interest; an increase/decrease in both of these factors has a similar influence to the main effect of the individual factors and would contribute to explaining the differences in magnitude between the coefficients of the screening and RPD models. However, in the event that A is increased and B decreased the interaction has an increasing effect on the overall VMD this is most likely due to an increase in the viscosity of the organic (dispersed) phase which is known to increases the VMD (*Polymerization Processes,* 1992). A correlation analysis of the interaction was conducted with the Statistica® software package which confirmed that there is a statistically significant negative correlation between the AB interaction and the organic phase viscosity.

The interaction AE (Mass UPR × Mass Water) indicates that for either an increase or decrease in both A & E there will an overall decreasing effect on the VMD which is most likely due to the disproportionate increase in A over E due to the difference in percentage change of the high and low levels (A = ± 13% & E = ±6%). However this interaction may have a significant influence on the real hold-up of the suspension.

The mechanism for the water pickup is believed to be temperature sensitive and therefore an interaction (AG) between the Mass polyester (A) & the Initial reactor temperature (G) would account for this temperature dependency. (The water pickup will affect the real hold-up and hence the VMD). The negative coefficient for this interaction appears to be correct; since an increase in both A & G would decrease the effective hold-up and vice versa.

The interaction (BG) effect between the Mass Styrene (B) and the Initial reactor temperature (G) exhibits no statistically significant correlation between any of the physical properties of the organic dispersed phase that were measured. This suggests that this interaction is most likely a modelled mathematical one to offset the VMD for the relative ratio between the factors B & G added to the formulation. However this could be an influence of the temperature on the Interfacial tension (IFT) of the sample as the temperature will also have a significant effect on the temperature sensitive IFT and hence influence the VMD.

Of interest is the interaction EG (Mass Water × Initial Reactor Temperature) as this was not observed in the screening design as it was confounded with the AD interaction. This interaction most likely has an effect on the effective hold-up of the suspension and therefore would account for the interaction's influence on the MVP. The negative relationship between the interaction EG and the VMD fits with the observation that the water pickup is greater at lower temperatures coupled with the lower continuous phase viscosity, reduces the shear; resulting in the reduction of the breakage rate.

The interaction effects AC, AD, BD & DG exhibited no statistically significant correlation between any of the physical properties of the organic dispersed phase that were measured. This suggests that the interactions are most likely just modelled mathematical terms to offset the VMD for the relative ratios between the interacting factors. However the AD interaction (Mass UPR × Mass DETA) may have a significant influence on the real hold up as per the theory discussed in chapter 4.6.1.

UPR Main & Interaction Effects Interpretation:

The UPR's characteristics, acid value (H) & viscosity (J), had the greatest effect contribution to the model of the factors analysed; contributing 4.60% & 24.77%, to the model respectively. The UPR factors, H & J, and their interactions (AH, BH, CH, DH, DJ, EJ, FJ, GH & HJ), effect contribution totalled 49.99%[1] to the modelled response variation. This confirms the observations by Terblanche (2002), Gous (2003) and Simpson (2010) that the UPR has an overwhelming influence on the VMD of the MVP and that any batch-to-batch variation in the UPR will have a significant effect on the VMD results.

A correlation analysis using Statistica® of factors H & J and their interactions, indicated that the acid value (H) had a significant correlation to the IFT and the organic phase's density; and the UPR's viscosity (J) had a statistically significant correlation to the organic phase's viscosity.

A hypothesis proposed by Terblanche (2002), that the interaction between the carboxylic acid groups on the UPR (quantified by the acid value) and DETA act as a surfactant to increase the water pick up

[1] Contribution to the model only not total variation (i.e. ignoring error).

of the MVP. The statistically significant correlation between the acid value (H)[1] and the IFT provide empirical support for this.

The UPR characteristics and their interactions' mechanisms are not well understood and therefore a mechanism will not be proposed as this is beyond the scope of this thesis.

5.5.2 Interpretation of the Buildup Model

The Buildup model selection and statistical validation has already been discussed in Chapter 5.4. From the ANOVA results for the Buildup (Table 5.9) the following interpretation of the model can be made:

The model is clearly significant with only a 0.01% chance that this result was due to noise. The significant lack-of-fit and the R^2 value of only 0.833 indicate that the model does not fit the experimental data as well as would be preferred but is still acceptable due to the subjective and interval nature of the data measurements.

The predicted variation of the response data (Pred R^2 = 0.654) explained by the model is not sufficient for highly accurate predictions but should be able to provide a ballpark figure for the Buildup response prediction.

Equation Comparison:

$$\begin{aligned}\ln(Buildup + 0.05) = -1.070 - 0.098A + 1.008B + 0.292C - 0.386D - 0.357E + 0.095F \\ -0.327G + 0.017H - 0.422J + 0.352AE - 0.319BE + 0.522BG + 0.365BH \\ +0.450CD - 0.430CH + 0.305DE + 0.477DH - 0.456EG - 0.322EH \\ +0.305EJ - 0.322FJ + 0.557GH - 0.329GJ \qquad (5.5)\end{aligned}$$

$$Buildup = 2.28 + 1.16B + 0.34C + 0.84D - 0.47E + 0.34F - 0.59G - 0.47L \qquad (4.3)^{2}$$

Unfortunately the two models where not directly comparable due to the transformation of the response used during the model development. However it should be noted that the Mass of UPR (A) (retained for hierarchy) was found to be insignificant for both models and the terms B - D & G were found to be significant for both models. It is worth noting that the models disagreed on the significance of the stirrer speed (F) as it was found to be significant in the screening model and not in the RPD model.

Whilst the magnitude of the coefficients cannot be compared the direction of the trend of the coefficients can be. All the coefficients between the two models agreed on whether the variables decreased or increased the Buildup response with the exception of the Mass of DETA (D) which was

[1] The interaction DH (Mass DETA × UPR Acid Value) had a statistically significant correlation to the IFT further adding support to this hypothesis.

[2] Variable references have been changed to be directly comparable to equation 5.5 – L refers to Mass CHP which was not included as a factor in the RPD Model.

determined to increase the Buildup in the screening design (equation 4.3) and predicted to decrease the Buildup with in the RPD model (equation 5.5).

Main Effect Interpretation:

The Mass Styrene (B) added to the formulation has an effect contribution of 26.61% and therefore, the greatest influence on the reactor Buildup. As mentioned in Chapter 4.6.2, this is most likely due to the styrene facilitating grafting between the HEC & PVOH of the continuous aqueous phase.

The Mass of LMA (C) added to the formulation was found to have an increasing effect on the Buildup for increasing quantities of LMA which is most likely due to the increasing of the effective hold-up through coarsening of the particles.

The Mass DETA (D) main effect in the RSM RPD model was found to decrease the Buildup for an increase in Mass DETA added to the formulation. This was in contradiction to the screening model where the reverse effect was observed and in contradiction to the mechanism discussed in chapter 4.6.2. The magnitude of the coefficient was half that of the coefficient for factor D in the screening model and therefore is most likely a mathematical term to offset the effect of the DETA incorporated in the interaction terms (discussed below).

An increase in the Mass of Water (E) has a decreasing effect on the Buildup. This was expected since the additional water decreases the reactor hold-up and dilutes the aqueous polymers reducing the probability of grafting occurring in the reactor.

The initial reactor temperature (G) was observed to have a reducing effect on the reactor Buildup. This may be due to the decreasing effect an increase in the temperature has on the water pickup of the organic droplets as observed through a decrease in the contrast ratio (vesiculation) with an increase in the initial temperature.[1]

The mass UPR (A) and stirrer speed (F) were found not to be statistically significant in its own right and was only retained to maintain the model's hierarchy due to the significant AE and FJ interaction effect.

2-Factor Interactions Interpretation:

It is difficult to clearly interpret 2-factor and higher order interactions of a model directly, particularly when each of the terms in the interaction participate in multiple interaction effects. However, if statistically significant correlations (Appendix E.3) can be found between interaction effects and the system's parameters, it is not unreasonable to interpret the correlations as the effect (but not cause) of the interaction terms.

The interaction between the Mass polyester (A) and Mass Water (E) was found to be significant (as expected) since a change in this ratio affects the reactor hold-up and hence the reactor Buildup. A similar interaction between the Mass water (E) & The Mass styrene (B) was found to affect the Buildup in the reactor, most likely due to the dilution of the PVOH & HEC reducing the effectiveness of grafting between these molecules.

[1] Refer to Chapter 4.6.2 for more detail.

There is a strong positive interaction between the Mass Styrene (B) and the initial reactor temperature (G). This is most probably due to the increase in solubility of styrene (Lane, 1946) in the aqueous phase with an increase in temperature which would result in a higher concentration of styrene in the aqueous phase and hence an increase in the occurrence of the grafting reaction between the styrene monomer and HEC & PVOH polymers. The interaction, EG, between the Mass water (E) and Initial temperature (G) had a reducing effect on the Buildup for a reduction in this value.

An interaction effect (CD) between the Mass LMA (C) and the Mass DETA (D) was found to have an increasing effect on the Buildup for an increase in this value. It has been hypothesised that the DETA aids in drawing the monomers into the aqueous phase increasing the grafting reaction (Paine, 1990; de Wet Roos, *personal communication,* 26 July 2010). Interesting to note is the interaction DE, this adds weight to the hypothesis that the DETA draws monomer into the aqueous phase accounting for the positive interaction between the DETA (D) and Water (E).

UPR Main & Interaction Effects Interpretation:

The UPR characteristics, acid value (H) & viscosity (J), did not have as large an effect contribution to the model as was previously thought (0.01% & 5.15% respectively). However once including their interaction terms (BH, CH, DH, EH, EJ, FJ, GH & GJ) the total influence of the UPR had an effect contribution to the model of 37.56%[1].Therefore the influence of the UPR on whether a batch may gel or not is highly dependent on the interaction with other factors and subsequently there should be significant room to select the factor levels to avoid a batch of UPR from causing Buildup/gelling in the reactor.

There was a statistically significant correlation between the interfacial tension and the Buildup suggesting that any effects that affect the IFT will have some effect on the Buildup. This was observed to be the case for the interaction DH which had a statistically significant correlation with the IFT which holds well for the theory that the DETA acts as a surfactant in conjunction with the carboxylic acid groups of the UPR (Terblanche, 2002). No other significant correlations were observed.

The UPR characteristics and their interactions' mechanisms are not well understood and therefore a mechanism will not be proposed as this is beyond the scope of this thesis.

[1] Contribution to the model only not total variation (i.e. ignoring error).

5.6 Model Verification & Optimisation

Several verification batches were run to verify the model and to predict an optimised formulation and process as follows:

- A standard MVP system for each of the four UPR batches (SCR-A01 – SCR-D01)[1].
- An optimised MVP system for each of the four UPR batches (SCR-A11 – SCR-D11)[1].
- Standard & optimised MVP system for two randomly produced UPR batches. (SCR-E01 - SCR-F01 and SCR-E11 - SCR-F11 respectively)[1].

The batches were compared to each other to determine if the optimised system reduced the influence of the UPR on the final MVP product.

5.6.1 Propagation of Error

$$PoE = \sqrt{V_z\left[y(x,z)\right]} = \sqrt{\sum_{i=1}^{r}\left[\frac{\partial y(x,z)}{\partial z_i}\right]^2 \sigma_{z_i}^2 + \sigma^2} \tag{5.6}$$

The Propagation of Error (PoE) model is represented by equation 5.6. All the equation terms can be calculated from the experimental data with the exception of the variance of the noise variable$\left(\sigma_{z_i}^2\right)$, this variance needs to be estimated by the experimenter. The estimates for the three noise variables are based upon the assumption that 95% of all the noise variation will fall within the design space:

- Initial Reactor Temperature: $\sigma_{z_G} = 3.75$
- UPR Acid Value: $\sigma_{z_H} = 5.79$
- UPR Viscosity: $\sigma_{z_J} = 98.25$

The experimental data was fitted to equation 5.6 and the model analysed using the Design Expert 7® software.

[1] The notation is as follows: First digit (A-F) refers to the UPR batch. The second digit refers to the formula (0 – Standard; 1 – Optimised). The last digit refers to the run number.

Figure 5.12 is a perturbation graph representing how the value of the PoE(Buildup) changes for a deviation in any of the model factors (A-J) from the standard system. The plot indicates that the PoE(Buildup) is most sensitive to variations in the Mass Styrene (B) added to organic phase.

Figure 5.12: Perturbation Graph for the PoE (Buildup) Model.

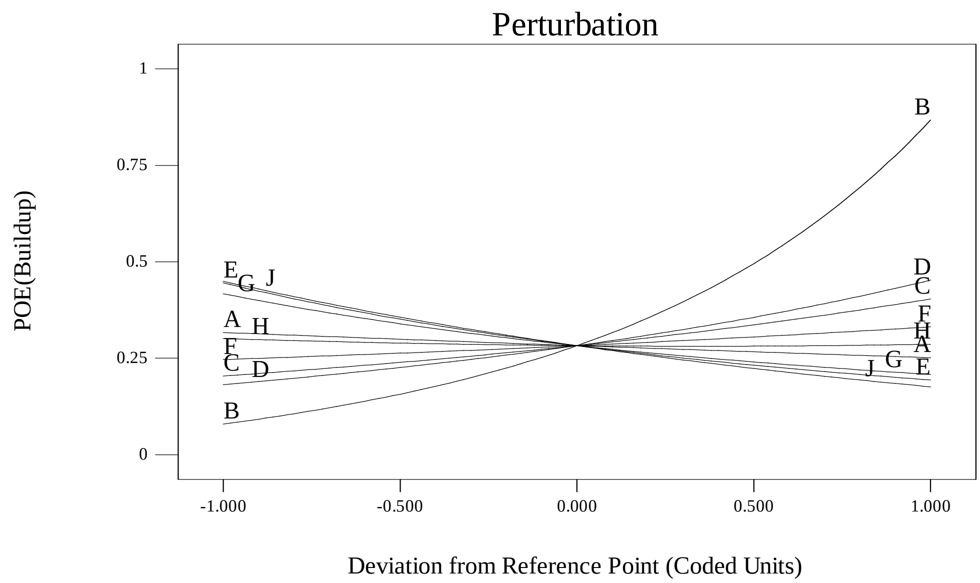
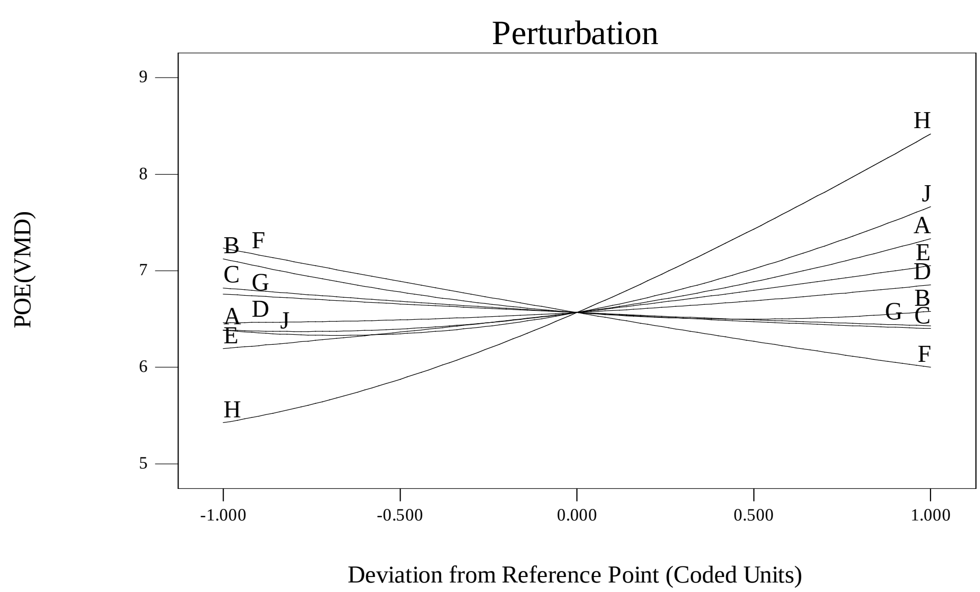


Figure 5.13 is a perturbation graph representing how the value of the PoE(VMD) changes for a deviation in any of the model factors (A-J) from the standard system. The plot indicates that the PoE(VMD) is most sensitive to variations in the UPR's acid value (H) followed by the UPR's viscosity (J). This experimentally validates the observation that any variation in the quality of the UPR has a significantly noticeable effect on the VMD of the MVP.

Figure 5.13: Perturbation Graph for the PoE (VMD) Model.



The significant variation in the PoE(VMD) for various factors in the design space suggests that there is the possibility for significant improvement in the MVP system through minimisation of the PoE(VMD).

Further investigation of the PoE(VMD) through optimisation of the process indicated that the VMD variation over the UPR's characteristics design space could be reduced from the standard (Figure 5.14a) to the optimised (Figure 5.14) MVP system. This corresponded to a reduction in the PoE(VMD) over the UPR design space as observed in Figure 5.15a to Figure 5.15b.

Figure 5.14: The VMD Variation over the UPR Design Space.

Figure 5.14a: Standard MVP System.

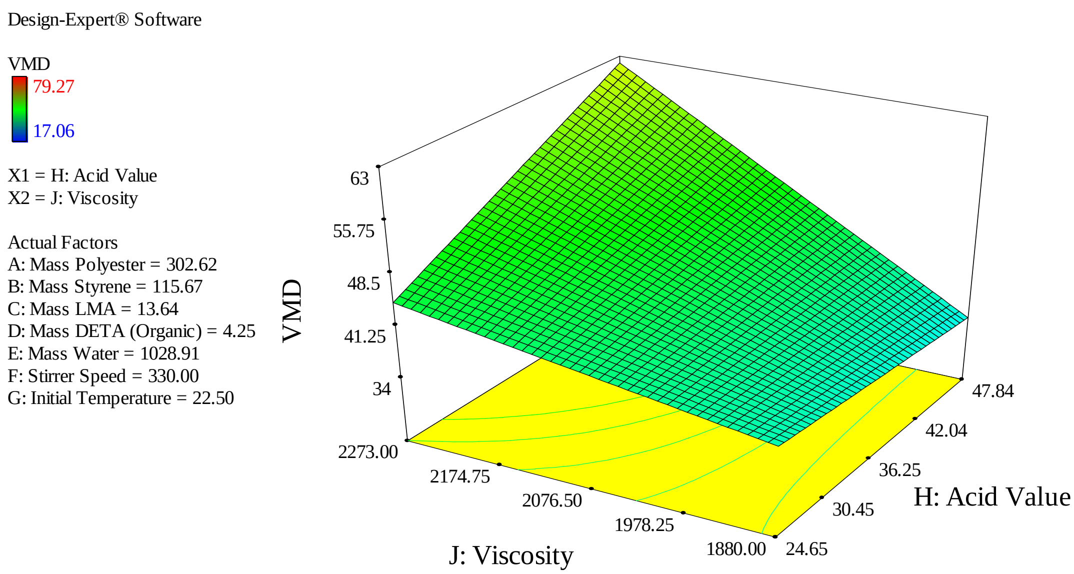


Figure 5.14b: Optimised MVP System.

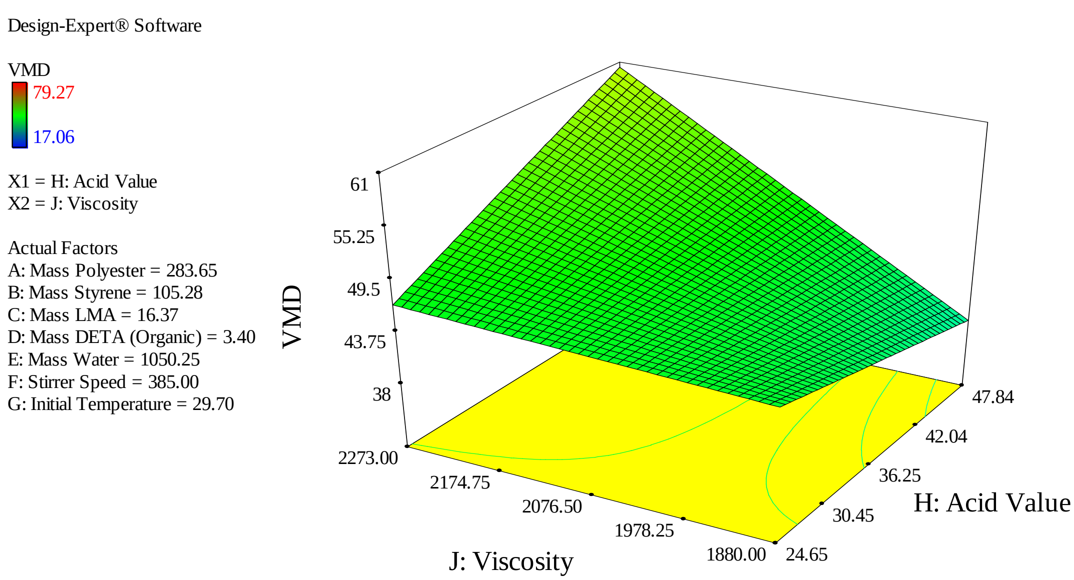


Figure 5.14 indicates that the VMD is more sensitive to variations in the UPRs' acid value than the UPRs' viscosity however the effect of the viscosity becomes more pronounced at higher acid values. A higher viscosity and/or acid value have an increasing influence on the VMD of the MVP. There is also less overall variation in the optimised system (figure 5.14b) than for the standard system (figure 5.14a). The optimised system brings the VMD variation closer to the desired mean of 47.5μm than the standard system.

Figure 5.15: The PoE(VMD) Variation over the UPR Design Space.

Figure 5.15a: Standard MVP System.

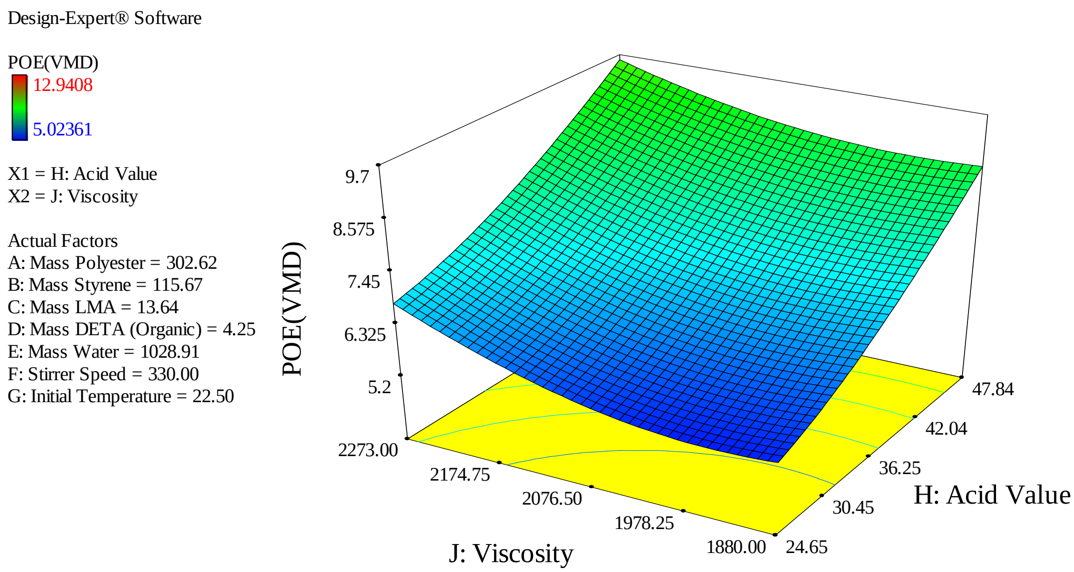
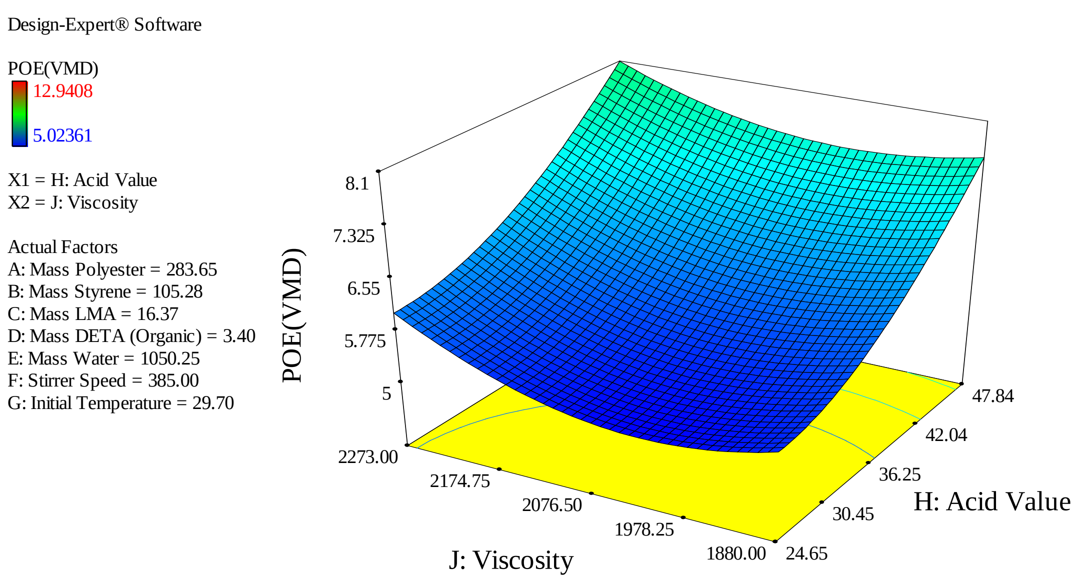


Figure 5.15b: Optimised MVP System.

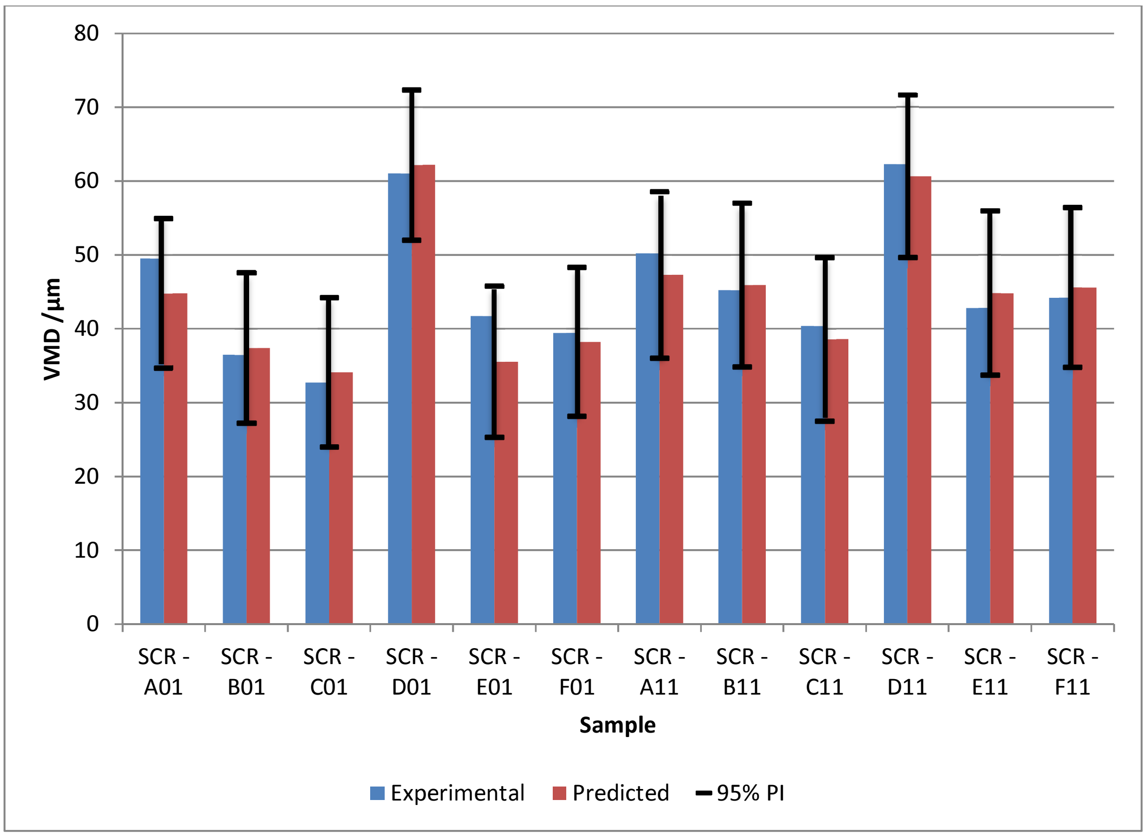


The overall PoE(VMD) is reduced by the optimised MVP system (Figure 5.15). The PoE(VMD) is lower for lower acid values suggesting that a more robust UPR can be obtained at lower acid values[1]. The reduced variation of the PoE(VMD) over the UPR's design space for the optimised MVP system confirms the reduced sensitivity of the optimised MVP system. The PoE(VMD) is less sensitive to the UPR's viscosity than it is to the UPR's acid value.

5.6.2 Model Verification

The 12 batches mentioned above were used to verify the VMD model (Figure 5.16), all of the samples fell within the 95% prediction interval (Table 5.10), experimentally validating the models suitability for predicting the VMD.

Figure 5.16: Verification Batches: VMD Predicted vs. Experimental.



The average percentage error for the verification batches' predicted VMD was 5.16%. Comparing the average prediction error, 2.16µm to the repeatability standard deviation[2] of 1.96µm, it can be seen that the prediction error is only slightly above the expected MVP batch-to-batch variation which suggests that the model has a high degree of accuracy for predicting the VMD.

[1] This has previously been observed in the work of the prior patents (Gunning et. al. (1972); Tioxide Group Ltd, 1981; Goldsbrough & Hodge, 1983; Karickhoff, 1984; Engelbrecht et. al., 2006) refer to Chapter 2.3.5

[2] The standard deviation of the 5 centre points of the screening design – estimate of repeatability error.

Table 5.10: Predicted vs. Experimental Verification Data (VMD).

Batch	Experimental /µm	Predicted /µm	95% PI Low /µm	95% PI High /µm	%error
SCR - A01	49.51	44.79	34.69	54.88	10.54%
SCR - B01	36.48	37.40	27.23	47.56	2.46%
SCR - C01	32.72	34.10	24.01	44.20	4.06%
SCR - D01	61.07	62.19	52.05	72.32	1.80%
SCR - E01	41.71	35.53	25.28	45.78	17.39%
SCR - F01	39.45	38.22	28.18	48.26	3.22%
SCR - A11	50.18	47.29	36.06	58.51	6.12%
SCR - B11	45.22	45.92	34.87	56.96	1.52%
SCR - C11	40.36	38.57	27.54	49.59	4.64%
SCR - D11	62.27	60.63	49.66	71.60	2.70%
SCR - E11	42.81	44.83	33.73	55.92	4.50%
SCR - F11	44.19	45.57	34.77	56.37	3.03%

5.6.3 Comparison of the Standard & Optimised MVP Systems

The Design Expert 7® software applies the Nelder-Mead downhill simplex method (Stat-Ease, 2005), to a desirability function to numerically optimise the desirability, based upon the optimisation criteria specified by the user. The desirability function (equation 5.7) is a geometric mean of the weighted average of the desirable range of each response.

$$D = \left(\prod_{i=1}^{n} d_i^{r_i}\right)^{\frac{1}{\sum r_i}} \tag{5.7}$$

The user specifies the optimisation criteria for the relevant responses and the software calculates the local maxima for the desirability function. To increase the probability that the design space maxima is found an initial 30 starting points for the numerical optimisation are chosen and the solutions are then displayed in order of magnitude of the desirability function.

To find a solution that was as independent of the UPR affects as possible the average UPR properties were used in the desirability function. The criteria in Table 5.11 were used to determine the optimised system.

Table 5.11: Optimisation Criteria.

	Criteria	Weight	Importance
UPR Acid Value	Target = 36.25	1	+++
UPR Viscosity	Target = 2076.5	1	+++
Buildup	Minimise	1	+++
%NVC	Maximise	1	+++
VMD	Target = 48	5	++++
PoE(VMD)	Minimise	5	++++
Cost /kg	Minimise	1	+++

The numerical solution recommended by the DX7® software is listed in Table 5.12. The optimised system has a notable decrease in the organic phase percentage as illustrated by the standard theoretical hold-up of ~0.245 compared to the optimised system's theoretical hold-up of only 0.232.

There is a notable decrease in the quantity of UPR and styrene in the formulation which should have an overall increasing effect on the VMD, particularly in conjunction with the increase in the quantity of LMA and increase in quantity of water. This was expected since the average VMD was increased from the standard's average of 44.6µm to the optimised's average of 48.1µm. It is interesting to note that the increase to the VMD would have been significantly greater if the stirrer speed was not increased drastically from 330 to 385rpm. Whilst this seams counter intuitive the effect on the MVP system is to reduce the PoE(VMD) as illustrated by the perturbation diagram (Figure 5.13); all the changes made to the system (with exception of Mass UPR (A) & Mass Water (E)) have a decreasing effect on the PoE(VMD) thus reducing the influence of the UPR's characteristics on the MVP properties whilst still meeting the required specifications for the MVP properties (Table 5.12).

Table 5.12: Comparison of Standard & Optimised MVP Systems.

	Component	***Standard***	***Optimised***
	Organic Phase		
1	Unsaturated Polyester	15.13%	14.23%
2	Titanium Dioxide Pigment	0.88%	0.88%
3	Styrene	5.78%	5.28%
4	Lauryl Methacrylate	0.68%	0.82%
5	Diethylene Triamine	0.21%	0.17%
	Aqueous Phase		
6	Water	51.45%	52.68%
7	Polyvinyl Alcohol Solution	13.13%	13.17%
8	Cellulose Thickener Solution	10.34%	10.37%
9	Diethylene Triamine	0.06%	0.06%
	Initiator System		
10	Water	0.21%	0.21%
11	Ferrous Sulphate	0.01%	0.01%
12	Cumene Hydroperoxide	0.12%	0.12%
	Post Treatments		
13	Surfactant	0.99%	0.99%
14	Water	0.38%	0.38%
15	Ammonia Solution	0.19%	0.19%
17	Thickener	0.19%	0.19%
18	Acticide	0.24%	0.24%
	Total	100.00%	100.00%

19	***Stirrer Speed***	330rpm	385rpm
20	***Initial Reactor Temperature***	22.5°C	29.7°C

Table 5.13 compares a standard & optimised MVP batch produced with a theoretical batch of UPR at the centre of the design space. Whilst some of the properties are outside of the current specification[1] the critical VMD characteristic is well within specification. Thus the thesis objective of reducing the sensitivity of the MVP system to the UPR characteristics is achieved whilst still meeting the specifications for the critical characteristic.

Table 5.13: Comparison of Theoretical MVP Batch Properties.

Property	Specification	Standard	Optimised
Non-volatile Content	23.5 – 24.5%	25.10%[2]	23.50%
Viscosity (Brookfield LVT #3/30rpm)[1]	2000-15000cP	904cP	822cP
pH	7.5-9.0	8.1	8.2
Particle Size (SMD)[3]	20-30µm	19.56µm	19.33µm
Particle Size (VMD)	35-60µm	44.56µm	47.84µm
Specific Gravity (wet)	1.040 – 1.050 kg/L	1.046kg/L	1.043kg/L

The sensitivity of the MVP to the UPR batch-to-batch variation was estimated theoretically and experimentally based upon batches of MVP made with the model UPRs A-D. Table 5.14 lists the descriptive statistic of these batches. It can clearly be seen that the sensitivity of the MVP system to the UPR variation was reduced by the reduction in the standard deviation for the VMD from 12.94µm for the standard system to 9.41µm for the optimised system. This reduction in standard deviation, coefficient of variation and the reduced VMD range indicates that the optimised system is less sensitive to the variation of UPR batch-to-batch variation. The decrease in variation is particularly noticeable by the decrease in CV by over one third. This reduction in variation is graphically represented in Figure 5.17. A hypothetical histogram (Figure 5.18) based upon the standard deviations and means of the data from Table 5.14 illustrates the improvement in the optimised system over the standard system (Refer to Chapter 3.2.2).

Table 5.14: Descriptive Statistics for MVP Systems Manufactured with a Range of UPRs.

	Standard		Optimised	
	Predicted	Experimental	Predicted	Experimental
Mean	44.62	44.95	48.10	49.51
Standard Deviation	12.53	12.94	9.19	9.41
Coefficient of Variance[4]	28.09%	28.78%	19.10%	19.00%
Range	28.08	28.35	22.06	21.91
Minimum	34.10	32.72	38.57	40.36
Maximum	62.19	61.07	60.63	62.27

[1] Most notably the Viscosity – this is not of concern as the post treatment thickener level can be optimised to compensate for this. (This is beyond the scope of this thesis).
[2] The standard batch failed to meet the %NVC specification.
[3] Whilst the results fall outside the specification it has already been indicated that the VMD is a better indicator of the effect of the Suede MVP's PSD on suede paint effect. Therefore it is recommended that the SMD no longer be used as means to specify the PSD of the Suede MVP.
[4] A method for comparing variance independent of the sample mean.

Figure 5.17: Comparison of MVP System Variation over a Range of UPRs.

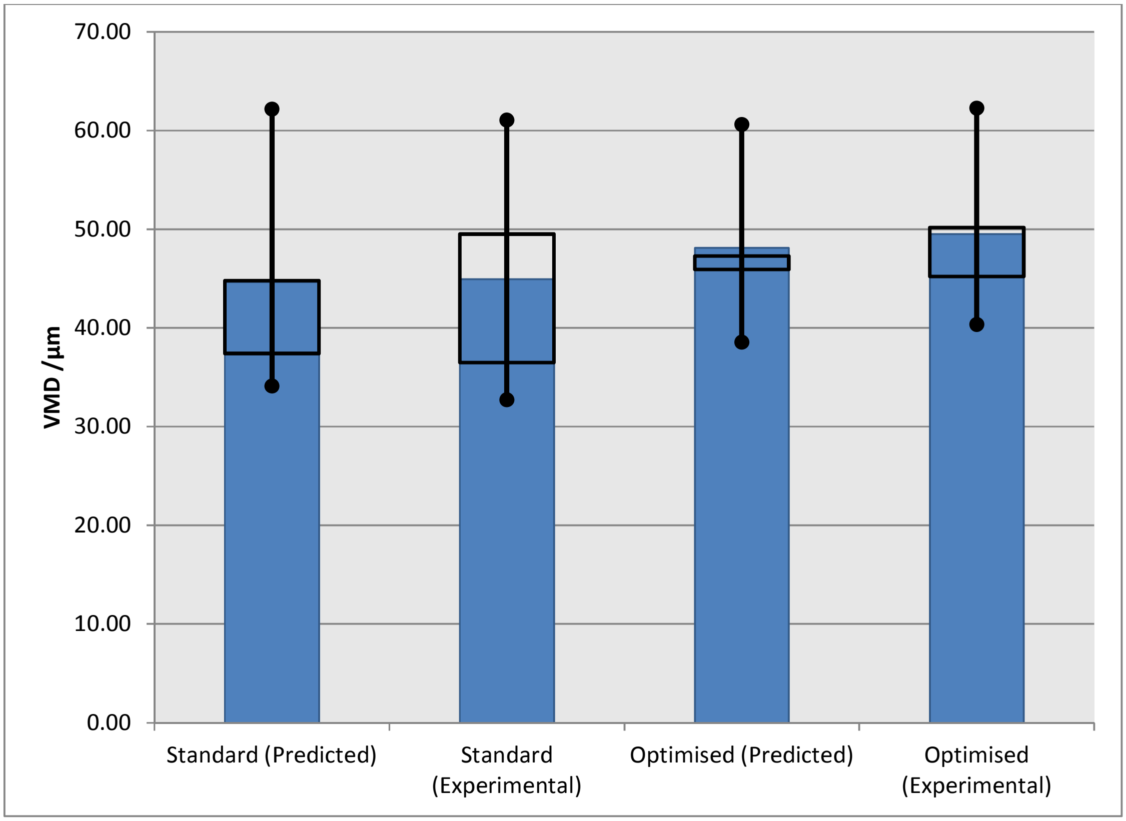
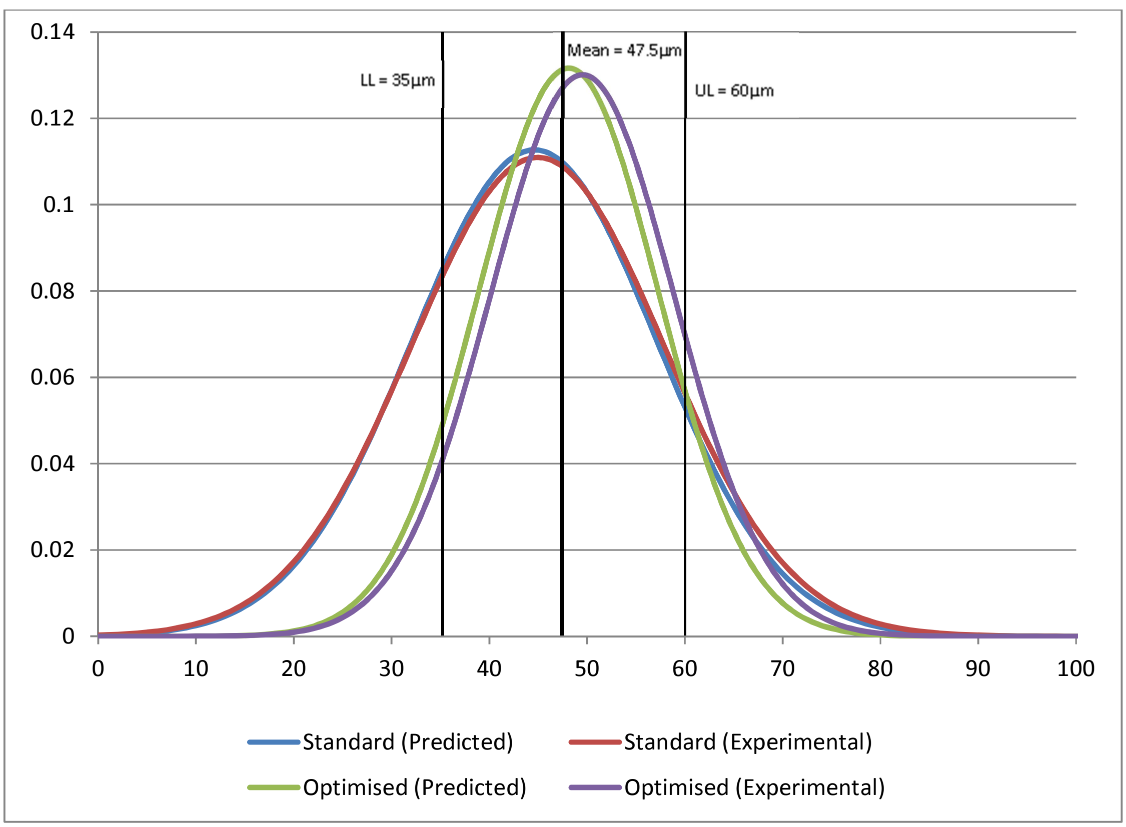


Figure 5.18: Hypothetical Histogram Comparing the Standard to the Optimised MVP System for the VMD.



5.7 Conclusion

A non-linear RPD model was successfully developed for the MVP system. This model was successfully used for minimising the sensitivity of the MVP system towards the UPR raw material with particular focus on the VMD.

- The model predicts the VMD and other properties with a high degree of accuracy as observed with the verification batches. (Appendix E.4).
- The sensitivity of the MVP system to the UPR design space was reduced by over 30% from the standard MVP system to the optimised system whilst still retaining the specifications of the MVP properties.
- The model had a high level of accuracy for predicting the VMD (Pred R^2 = 0.839) with an average error of 5.16% in the predicted verification batches.

Propagation of error was successfully used to estimate how the UPR effects the MVP VMD variations and how this influence can be reduced through correct selection of the factor levels.

- The RPD model results supported the observation that the UPR had a significant effect on the VMD with a total effect contribution to the model of 49.99%
- The PoE(VMD) is lower for lower acid values suggesting that a more robust UPR can be obtained at lower acid values. This was observed and noted in several of the previous patents (Gillian & Kershaw, 1969; Gunning et. al., 1972; Tioxide Group Ltd, 1981; Goldsbrough & Hodge, 1983; Karickhoff, 1984) which all indicated that it was preferable for the UPR to have a low acid value in the applicable range.
- An optimised formulation was developed which reduced the variation of the VMD with the UPR and brought the average VMD to within specification.

5.8 Nomenclature

Latin Variable	**Description**	**Units**
A	Mass UPR	-
B	Mass Styrene	-
C	Mass LMA	-
D	Mass DETA (organic)	-
	Desirability	-
D	Factor desirability	-
E	Mass Water	-
F	Stirrer speed	-
G	Initial reactor temperature	-
H	UPR acid value	-
J	UPR viscosity	-
L	Mass CHP	-
N	Number of design points	-
R_i^2	Coefficient of determination	-
R	Weight	-
Tr	Trace	-
V[ ]	Variance function	-
X	Design's control factor matrix	-
X	Control factor	-
Y	Response variable	-
y'	Transformed response variable	-
Z	Noise factor	-
Greek Variables	**Description**	**Units**
Β	Control factor regression coefficient	-
Γ	Noise factor regression coefficient	-
Δ	Control × noise factor regression coefficient	-
Δy	Desired signal strength	-
Ε	Error	-
Σ	noise	-
	Standard deviation	-

Subscript	**Description**	**Subscript**	**Description**
0	Mean	i,j,k	Generic subscript
Z	Noise factor		

6 Dimensional Analysis

6.1 Introduction

> "Dimensional analysis is based upon the recognition that a mathematical formulation of a chemical or physical technological problem can be of general validity only if it is *dimensionally homogenous"*
>
> \- Marko Zlokarnik (2006)

Dimensional analysis has previously been used to empirically model suspension polymerisation systems and, specifically the MVP system (Refer to Chapters 2.4.2.1 & 2.4.3 respectively). These models however are not directly applicable to the low-shear mixing system and formulation of the Suede MVP and therefore an empirical dimensionless model needs to be developed from scratch rather than fitting an existing model to the experimental data.

The most common form for the modelling of experimental data using dimensional analysis is to create dimensionless groups and determine the mathematical relationship between the dependent dimensionless groups as a function of the independent dimensionless groups as in this case using the Buckingham-Π method.

6.2 Model development

6.2.1 Buckingham Π Method

The Buckingham-Π method takes a dimensionally homogenous system of (n) parameters and reduces it to a smaller set of (n-p) dimensionless groups for analysis, were (p) is the number of dimensions (e.g. length or mass). These dimensionless (semi-)empirical models in conjunction with the principles of similitude are readily useable for the scaling-up or scaling-down of processes.

Table 6.1 lists the identified physical, geometric, & operating parameters that have an influence on the multi-vesiculated particles system. The identified dimensions were length (meters), time (seconds) & mass (kilograms). The system was assumed to not be dependent on temperature given that any variation in the temperature will be accounted for by the change in the physical properties of the system and the temperature of the system remained constant during the particle formation phase and was only increased after the identification point of the particles.

Table 6.1: System Parameters.

Geometric:				
Reactor Diameter	d (m)		Number of Baffles	N_b
Impeller Diameter	D (m)		Number of impellers	N_i
Height of stirrer above the reactor base	h (m)		Volume to Surface area ratio of the reactor	a ($m^3.m^{-2}$)
Operating:				
Stirrer Speed	N (s^{-1})		Batch (Emulsification) Time	t (s)
Power Input	P ($kg.m^2.s^{-3}$)		Hold-up Ratio	ϕ
Fluid Height	H (m)		Average Particle Size (VMD)	α (m)
Physical Characteristics:				
Dispersed Phase Density	ρ_d ($kg.m^{-3}$)		Continuous Phase Density	ρ_c ($kg.m^{-3}$)
Dispersed Phase Viscosity	μ_d ($kg.m^{-1}.s^{-1}$)		Continuous Phase Viscosity	μ_c ($kg.m^{-1}.s^{-1}$)
Interfacial Tension	σ ($kg.s^{-2}$)		Acceleration of Gravity	g ($m.s^{-2}$)

Essentially, the Buckingham Π method will be used to develop an equation which will have its parameters regressed from the experimental data of Chapter 5 to determine the VMD as a function of the above parameters (Table 6.1):

$$\alpha = f(d, D, h, N_b, N_i, a, N, P, H, t, \phi, \rho_d, \rho_c, \mu_d, \mu_c, \sigma, g) \tag{6.0}$$

Applying the Buckingham Π method to the above identified dimensional analysis (Appendix F.3) and using the dimensions D (m), N (s^{-1}) ρ_d ($kg.m^{-3}$) as the primary variables for the model the following equation was developed:

$$\left(\frac{\alpha}{D}\right) = k\left(\frac{d}{D}\right)^b\left(\frac{D}{D}\right)^c\left(\frac{h}{D}\right)^e(N_b)^f(N_i)^l\left(\frac{a}{D}\right)^m\left(\frac{N}{N}\right)^n\left(\frac{P}{N^3D^5\rho_d}\right)^p\left(\frac{H}{D}\right)^q(tN)^r(\varphi)^s\left(\frac{\rho_d}{\rho_d}\right)^u\left(\frac{\rho_c}{\rho_d}\right)^q$$

$$\times\left(\frac{\mu_d}{ND^2\rho_d}\right)^w\left(\frac{\mu_c}{ND^2\rho_d}\right)^x\left(\frac{\sigma}{N^2D^3\rho_d}\right)^y\left(\frac{g}{N^2D}\right)^z \tag{6.1}$$

If the PSD has reached a dynamic equilibrium after the emulsification period and before catalysis the PSD will be independent of the emulsification time and (tN) will become constant. Also catering for geometric similarity and using the same scale reactor, equation 6.1 reduces to:

$$\left(\frac{\alpha}{D}\right) = k(N_i)^l\left(\frac{P}{N^3D^5\rho_d}\right)^p(tN)^r(\varphi)^s\left(\frac{\rho_c}{\rho_d}\right)^q\left(\frac{\mu_d}{ND^2\rho_d}\right)^w\left(\frac{\mu_c}{ND^2\rho_d}\right)^x\left(\frac{\sigma}{N^2D^3\rho_d}\right)^y\left(\frac{g}{N^2D}\right)^z \tag{6.2}$$

Rearranging equation 6.2 and substituting in engineering dimensionless numbers results in:

$$\left(\frac{\alpha}{D}\right) = k\left(\frac{ND^2\rho_d}{\mu_d}\right)^a\left(\frac{N^2D^3\rho_d}{\mu_d}\right)^b\left(\frac{P}{N^3D^5\rho_d}\right)^e\left(\frac{N^2D}{g}\right)^f\left(\frac{\rho_c}{\rho_d}\right)^g\left(\frac{\mu_c}{\mu_d}\right)^h\phi^i \tag{6.3a}$$

$$\left(\frac{\alpha}{D}\right) = kRe_d^aWe_d^bNe_d^eFr^f\left(\frac{\rho_c}{\rho_d}\right)^g\left(\frac{\mu_c}{\mu_d}\right)^h\phi^i \tag{6.3b}$$

This equation is comparable to equation 2.5 developed by Langner et. al. (1980) for suspension polymerisation systems.

6.2.2 Parameter measurements

The system parameters in the model were obtained as follows:

1. The stirrer speed (N) was read off the IKA Eurostar-ST PCV P1 lab mixers.
2. The reactor geometry was measured directly from the vessels.
3. The density (ρ), VMD (α) & Interfacial tension (σ) were measured as discussed in chapter 3.5.1, 3.5.8 & 3.5.10 respectively.
4. The reactor holdup ratio (ϕ):
   Only the theoretical reactor holdup ratio was calculated as per equation 3.9 (Chapter 3.5.5). As discussed in chapter 2.2 one of the novel attributes of the MVP system is its ability to draw the aqueous phase into the organic phase to form vesicles. The drawing of the aqueous phase into the organic phase effectively reduces the volume of the continuous phase and increases the volume of the dispersed phase. This phenomenon increases the effective holdup and to date there has been no successful method for measuring this increase and therefore only the theoretical reactor holdup ratio can be calculated and used in this model.
5. The apparent viscosity (μ):
   Rheology flow curves of the dispersed and continuous phases were measured in line with the method of chapter 3.5.9. However both these phases exhibited non-Newtonian behaviour below shear rates of $10s^{-1}$ for the aqueous phase and below $100s^{-1}$ - $1000s^{-1}$ for the organic phase with Newtonian behaviour above these shear rates.
   According to Uhl & Gray (1986) the average shear rate in the impeller zone can be calculated as follows:

$$\dot{\gamma}_{av} = kN \tag{6.4}$$

   where for open impellers $k \approx 12$ (Uhl & Gray, 1986). (For a range of stirrer speeds of between 4.95-6.77rps the shear rate ranges from 59.4 – $81.2s^{-1}$).

   Therefore the apparent viscosity for the organic and aqueous phases for a given stirrer speed can be determined using equation 6.4 and the rheology flow curves of the phases.

6.2.3 Experimental Data Fitting

Not all physical parameters of each batch from the RPD DoE were measured and therefore the dimensional model was based upon a subset of 44 experiments (Appendix F.1).

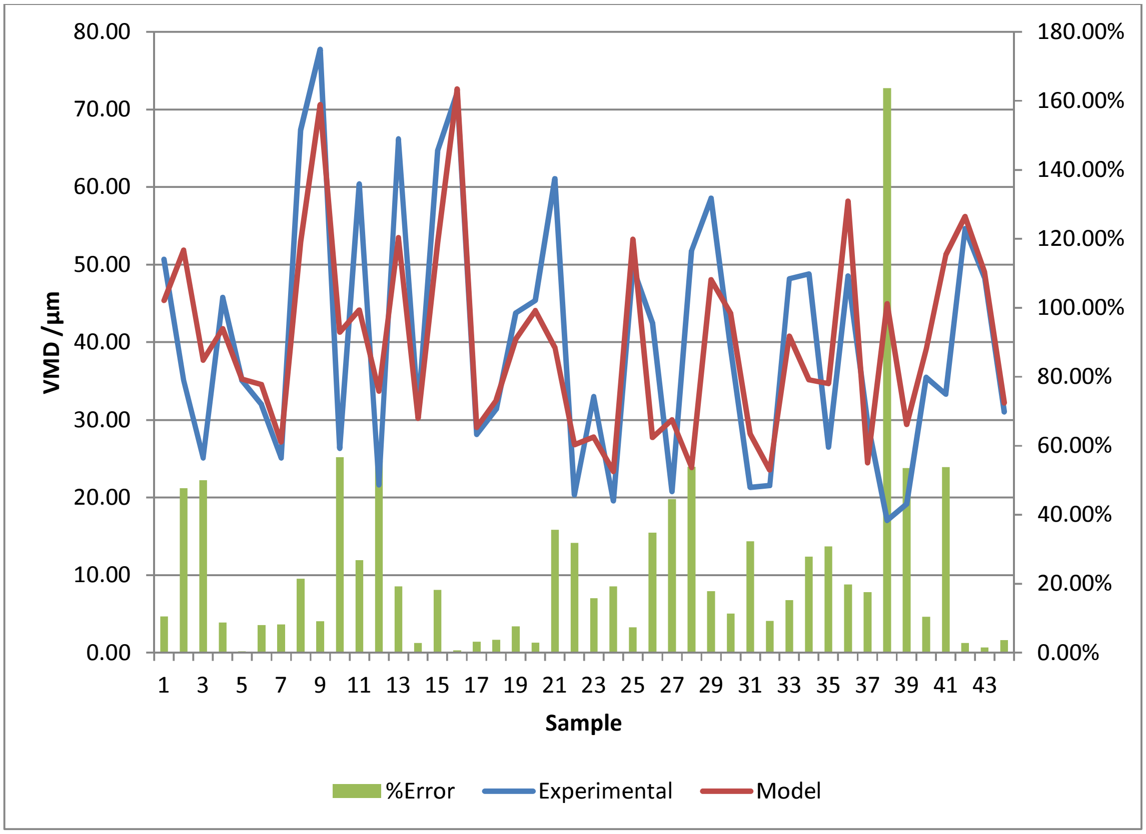
The coefficients for equation 6.3 were regressed using MatLab® (Appendix F.2) with the data measured from the experimental runs of the RPD experimental design and resulted in equation 6.5[1]:

$$\left(\frac{\alpha}{D}\right) = 7.77 \times 10^{-5} Re_d^{-8.21\times10^{-4}} We_d^{-0.186} Fr^{-0.298} \left(\frac{\rho_c}{\rho_d}\right)^{-10.39} \left(\frac{\mu_c}{\mu_d}\right)^{-0.331} \phi^{-1.218} \tag{6.5}$$

Figure 6.1 compares the experimental value of the VMD to the Dimensionless Model (DM) prediction of the VMD. The average error from the model prediction was 24.48% however errors in estimating the VMD were as high as 163.71%.

[1] The power input to the reactor was not measured and therefore the Newton number was removed from equation 6.3.

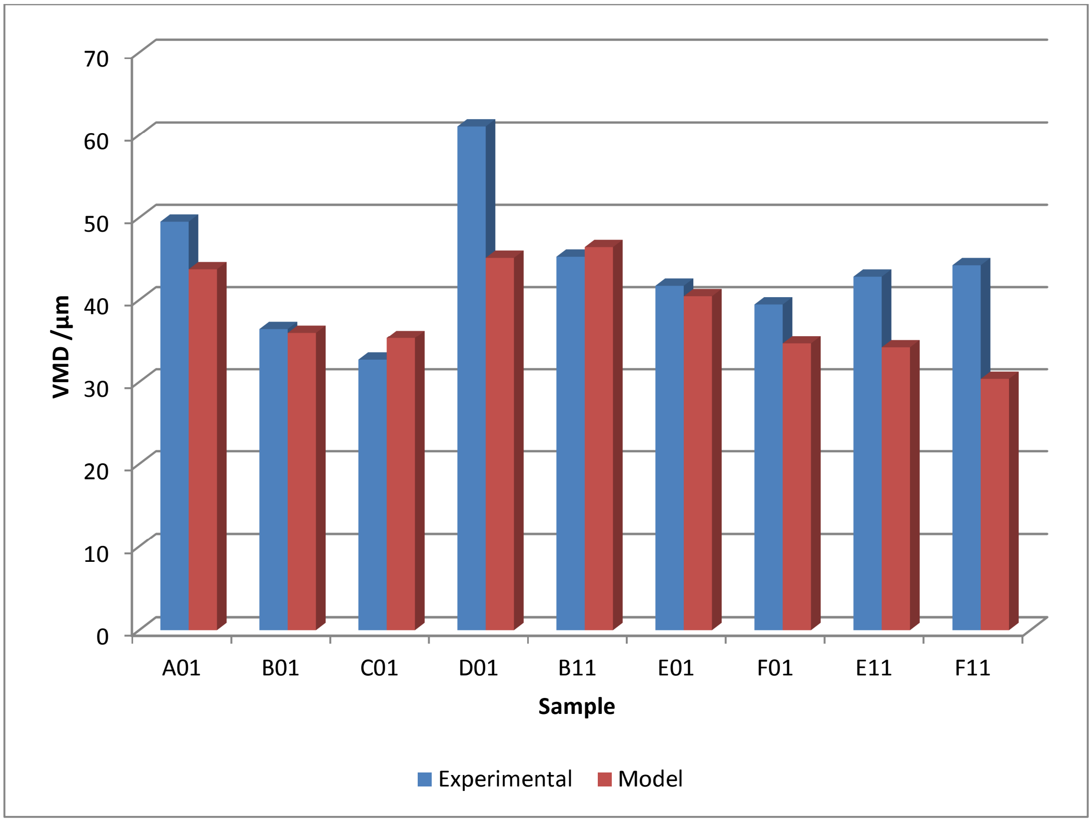
Figure 6.1: Equation 6.5 Predicted vs. Experimental values for the VMD.



6.2.4 Model Validation

Figure 6.2 compares the experimental value of the VMD to the DM prediction of the VMD for the validation experiments from Chapter 5.6. The average error for the model prediction was 12.92% however errors in estimating the VMD were as high as 31.25% (SCR-F11).

Figure 6.2: DM (Equation 6.5) Predicted vs. Experimental values of the VMD for the Verification Batches.



6.3 Models from Literature

None of the empirical models discussed in Chapters 2.4.2.1 & 2.4.3, are directly applicable to the Suede MVP suspension polymerisation system. They can however, be modified to apply to this system through model parameter regression for comparison to equation 6.5.

6.3.1 Suspension Polymerisation Models

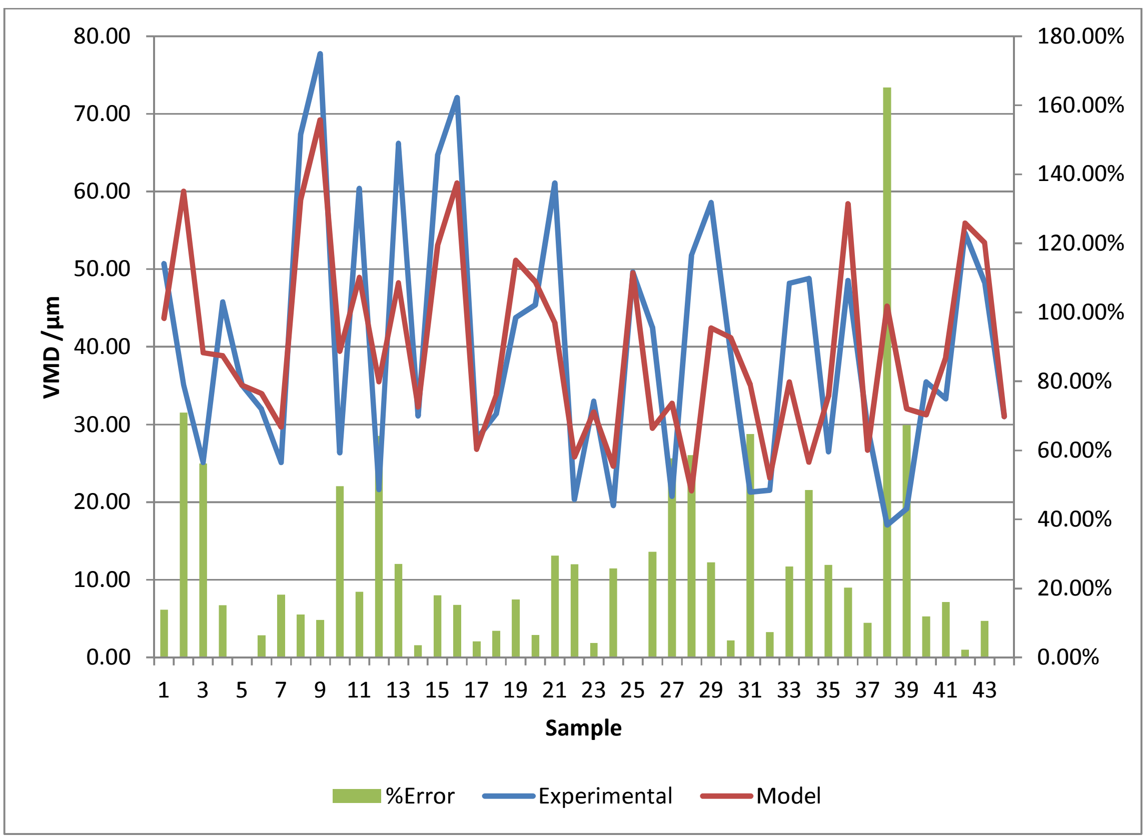
Hopff et. al. (1964) developed a model only applicable to a MMA suspension polymerisation with PVA stabilisers (equation 2.7). The Suede MVP whilst using a combined PVA & HEC stabiliser system, however, has a dispersed phase very dissimilar to the MMA dispersed phase.

$$ {d_{p_{50}}}/{D} = K Re^{1/2} We^{-1} \left(\frac{\mu_d}{\mu_c}\right)^{0.1} \tag{2.7} $$

However Hopff et. al. (1964) model was modified (equation 6.6) and new parameters calculated to fit the model to the MVP experimental data. The average error for this model prediction was 26.83% however errors in estimating the VMD as high as 165.19% were obtained.

$$ {\alpha}/{D} = 0.04928 Re^{-0.42} We^{-0.2617} \left(\frac{\mu_d}{\mu_c}\right)^{-0.01058} \tag{6.6} $$

Figure 6.3: Equation 6.6 Predicted vs. Experimental values for the VMD.



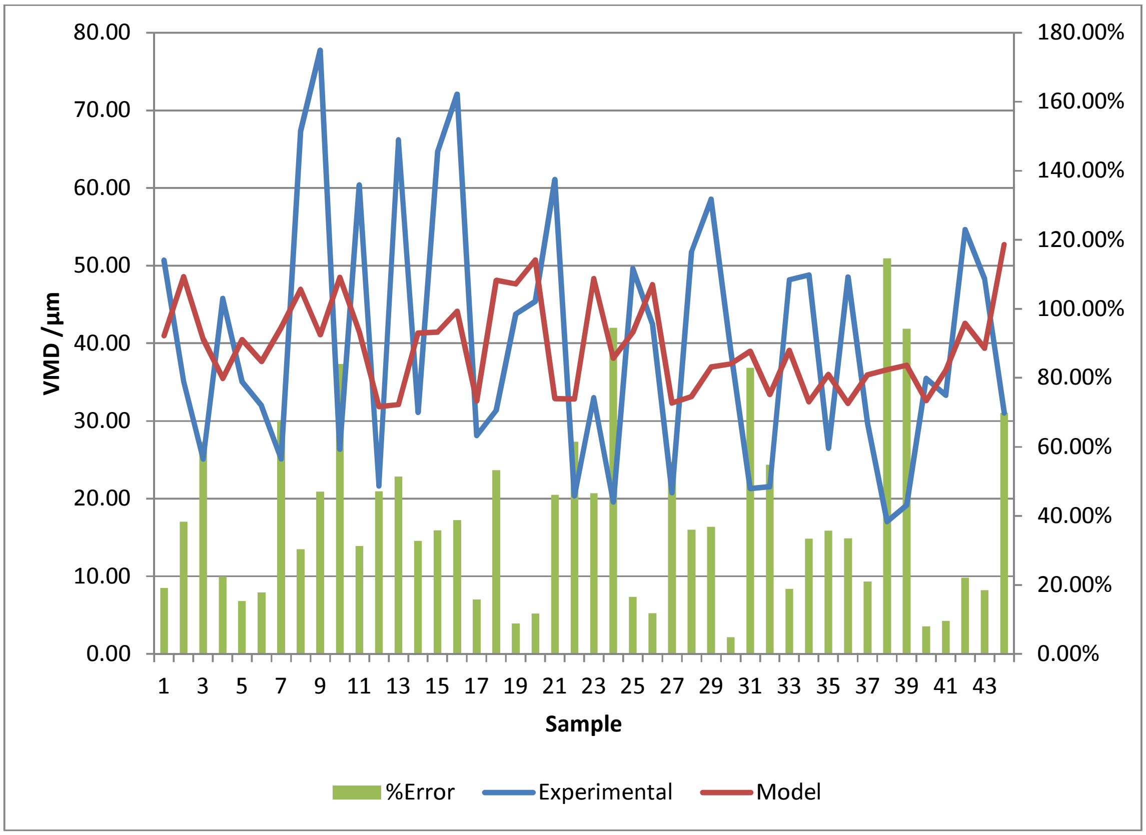
Arai et. al. (1977) developed a model for systems with a viscous dispersed phase which is dependent on the reactor scale (equation 2.8). Equation 2.8 relies on the continuous phase properties in contrast to the other methods which rely on the dispersed phase properties.

$$d_{p_{max}}/D = K\left(\frac{\rho_c N d^2}{\mu_c D}\right)^{-0.75} \tag{2.8}$$

Parameters were calculated for equation 2.8 to fit the model to the experimental data resulting in equation 6.7. The average error for the model prediction was 39.97% however errors in estimating the VMD were as high as 114.64%.

$$\alpha/D = 2.6773\left(\frac{\rho_c N d^2}{\mu_c D}\right)^{-0.75} \tag{6.7}$$

Figure 6.4: Equation 6.7 Predicted vs. Experimental values for the VMD.



Chatzi et. al (1989) reported a generalised correlation model, in the form of equation 2.9. The equation was used to predict the Sauter-mean Diameter (d_{32}) for a range of experiments with very good results, however the equation was only applied to systems of very low (0.01-0.03) holdup ratios, ϕ. The Suede MVP system has holdup ratios an order of magnitude higher than the reported applicable region for this model.

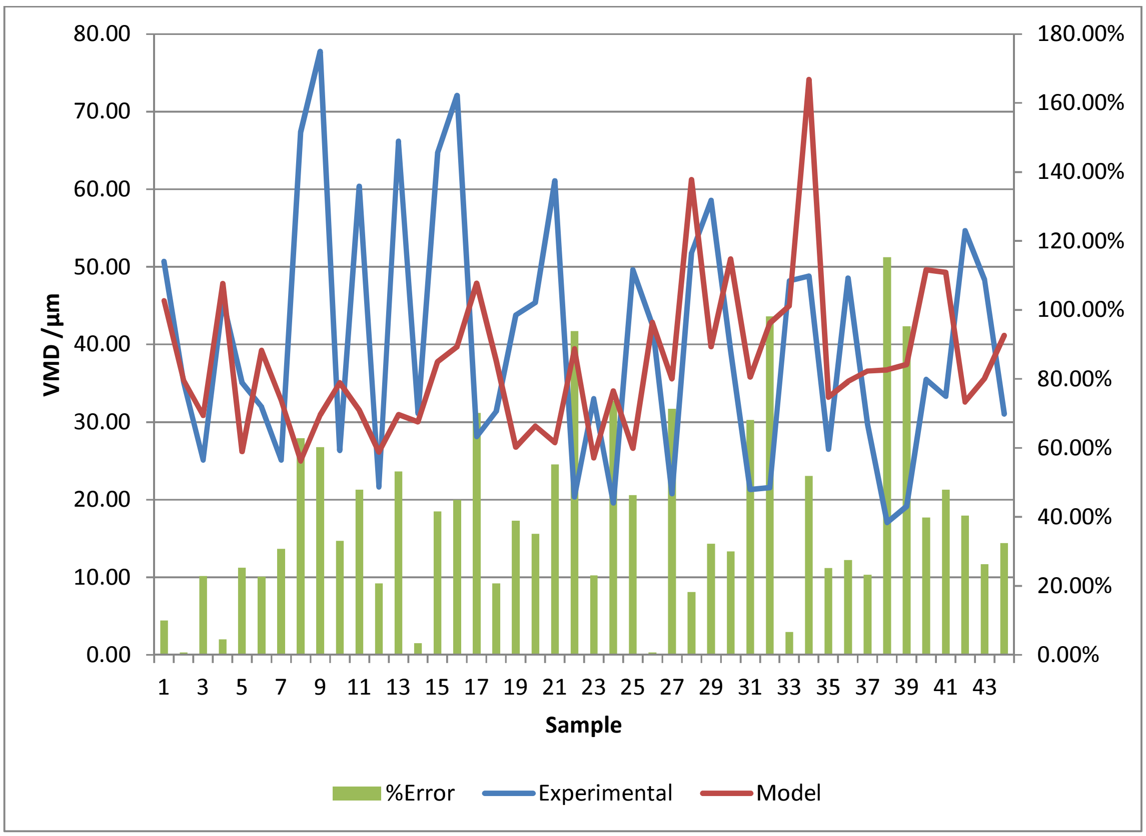
$$ {}^{d_{32}}/_{D} = a(1 + b\phi)(We_T)^{-c} \tag{2.9} $$

Were c is often considered to be 0.6.

Parameters were calculated for equation 2.9 to fit the model to the experimental data resulting in equation 6.8. The average error for the model prediction was 40.73% however errors in estimating the VMD were as high as 115.29%.

$$ {}^{\alpha}/_{D} = 1.13 \times 10^{-4}(1 - 2.6671\phi)(We_T)^{0.2966} \tag{6.8} $$

Figure 6.5: Equation 6.8 Predicted vs. Experimental values for the VMD.



6.3.2 Prior MVP Particle Size Model

The model (equation 2.15) developed by Terblanche (2002) was developed for a saw-tooth blade mixer and is therefore not applicable for the low-shear batch reactor used in for the work in this thesis due to the violation of the assumption of geometric similarity.

$$\alpha_t^{-1} = 0.63N^{0.76}D_i^{0.58}\left({D_i}/{d_t}\right)^{1.01} \tag{2.15}$$

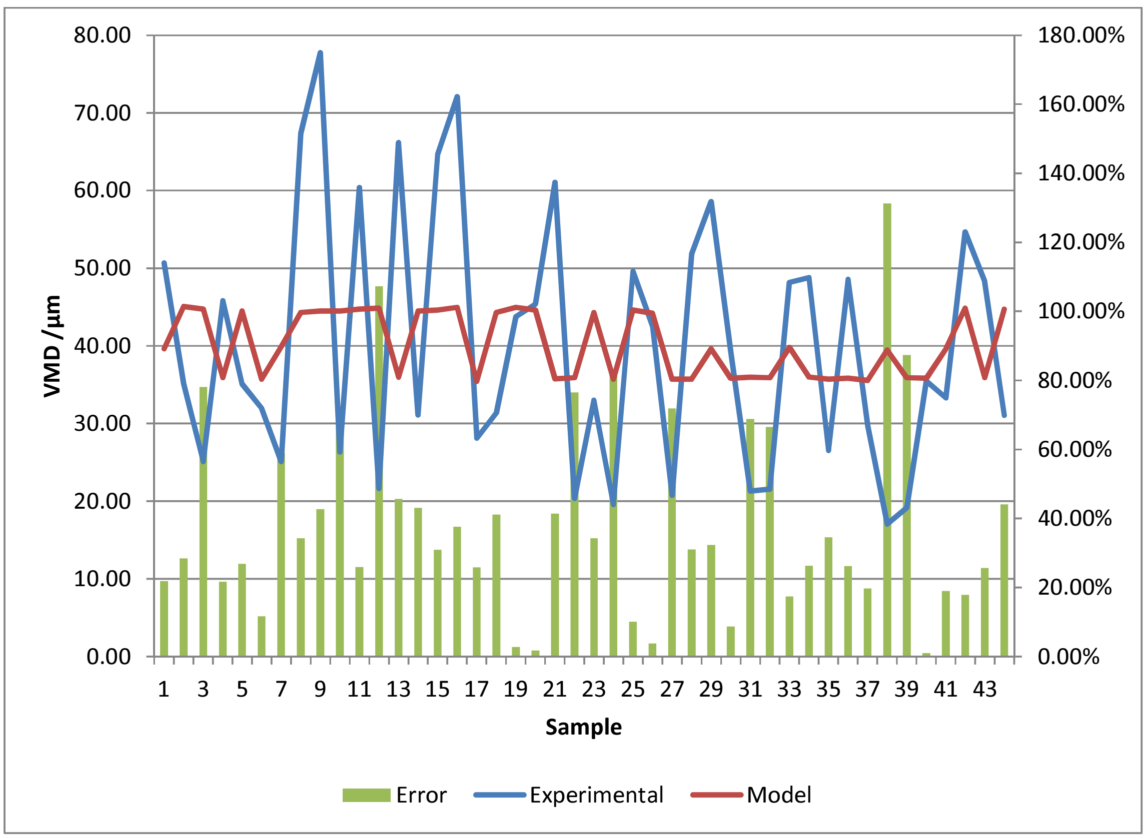
Terblanche's (2002) model is largely dependent on the geometry of the reactor and models how the particle size varies with a change in geometry and stirrer speed. The data generated, to model, the Suede MVP system was gathered on only the 2L scale equipment and therefore D_i & d_t are constant for all the experiments; consequently the model simplifies to equation 6.9 where the particle size is a function of only the stirrer speed (N).

$$\alpha_t^{-1} = k'N^a = 0.00645N^{0.7722} \tag{6.9}$$

Regardless of the simplification of Terblanche's (2002) model, for completeness of this thesis, the simplified model was fitted to the experimental data.

The average error for the model (equation 6.9) prediction was 39.40% however errors in estimating the VMD were as high as 131.29%. The oversimplification of Terblanche's model is evident in the high error for the prediction of the VMD.

Figure 6.6: Equation 6.9 Predicted vs. Experimental values for the VMD.



6.4 Model Comparison

6.4.1 Dimensional Analysis Empirical Model Comparison

Table 6.2: Model Comparison.

Model	Source	Error (Incl. outlier SCR-253)			Error (Excl. outlier SCR-253)		
		R^2	Average	Maximum	R^2	Average	Maximum
Equation 6.5	Buckingham-Π method	0.54	24.48%	163.71%	0.59	21.25%	56.67%
Equation 6.6	Hopff et. al. (1964)	0.45	26.83%	165.19%	0.50	23.61%	70.97%
Equation 6.7	Arai et. al. (1977)	-0.04	39.97%	114.64%	-0.06	38.23%	94.51%
Equation 6.8	Chatzi et. al (1989)	-0.39	40.73%	115.29%	-0.43	39.00%	98.13%
Equation 6.9	Terblanche (2002) – simplified	0.07	39.40%	131.29%	0.06	37.26%	107.28%

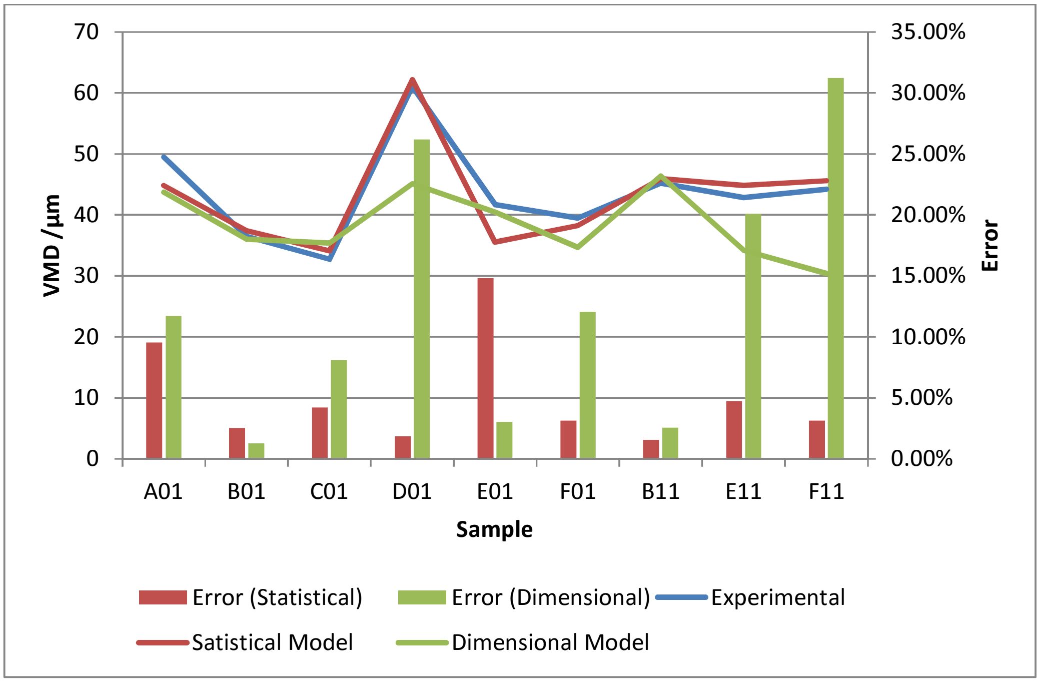
Table 6.2 lists the errors associated with the dimensional analysis empirical (DAE) models from literature including the model developed using the Buckingham-Π method. The model equation 6.5 developed using the Buckingham-Π method predicted the VMD with the least amount of error and had the highest coefficient of determination (R^2) of 0.59; however the error was still too high and the R^2 value too low, than would be required for accurate modelling of the VMD.
Model equations 6.7, & 6.8 all had a negative R^2 value indicating that the mean of the sample population would be a better estimate of the VMD data than the models themselves and are therefore not suitable for modelling the Suede MVP's VMD.

The only other model which could be considered to model the data sufficiently was equation 6.6, the modified equation of Hopff et. al. (1964). However the R^2 value of 0.45 was too low with too high an average error for accurate predictions of the VMD.

6.4.2 Comparison to the RPD Model

The DM model developed to predict the VMD of the Suede MVP was not ideal as it only had a R^2 of only 0.59 which does not compare well to the RPD model developed in Chapter 5 which had a R^2 value of 0.94. The DM model's inadequacies are further highlighted by the higher average model error for the verification batches of 12.92% whilst the RPD model had an average error of only 5.16%. Figure 6.7 clearly illustrates the superiority of the RPD model of Chapter 5 over the DM model of Chapter 6.

Figure 6.7: Model Comparison: RPD Model vs. DM Model.



6.5 Concluding Remarks

The DM model falls short of the required accuracy that is considered necessary for practical use of the model for predicting the VMD of the MVP system. There are several possible reasons for this:

- The error in using the theoretical holdup rather than the effective holdup.
- The error in measuring the IFT as the IFT tends to fall along the limits of the Du Noüy ring measuring range.
- There is expected to be significant error in the method used to estimate the shear rate and hence apparent viscosity particularly for the dispersed phase.
- The effect of the power input to the system was not considered.

Considering these concerns in future model development work should have a significant effect on reducing the model prediction error and improving the model fit.

6.6 Nomenclature

Latin Variable	**Description**	**Units**
a	Volume to surface area ratio	$m^3.m^{-2}$
a, b, e, f, g, h, I, j, K, k, l, m, n, o, p, q, r, s, u,	Model coefficients	-
D	Impeller diameter	M
d	Reactor Diameter	M
Fr	Fraude number	-
g	Acceleration of gravity	$m.s^{-2}$
H	Fluid height	M
h	Height of stirrer blade	M
N	Stirrer speed	s^{-1}
N_b	Number of baffles	-
N_s	Number of stirrer impellers	-
n	Number of parameters	-
P	Power input	$kg.m^2.s^{-3}$
p	Number of dimensions	-
Re	Reynolds number	-
t	Bach time	S
We	Weber number	-
Greek Variables	**Description**	**Units**
α	Particle size	M
$\dot{\gamma}_{av}$	Average shear rate	s^{-1}
μ	Viscosity	$kg.m^{-1}.s^{-1}$
ρ	Density	$kg.m^{-3}$
σ	Interfacial tension	$kg.s^{-2}$
ϕ	Hold-up ratio	-

Subscript	**Description**	**Subscript**	**Description**
50	50^{th} percentile	c	Continuous
d	Dispersed	i	Impeller
max	Maximum	p	Particle
T	Turbulent		

7 Conclusions & Recommendations

7.1 Introduction

The development of multi-vesiculated particles (MVP) by Freeworld Plascon South Africa and the University of Stellenbosch added a new weapon to the arsenal of the paint formulation chemist. However the insufficient understanding of the effect of the MVP system parameters on the final product, coupled with the MVP's sensitivity towards the unsaturated polyester resin (UPR) resulted in a product with significant quality variation. On the other hand these uncertainties provided the opportunity to model and optimise the MVP system. With this in mind the objectives of this thesis were:

- To create a better understanding of the contribution of each system parameter to the MVP product.
- To develop an empirical model which could be used to optimise the MVP system.
- To select the MVP system's parameters to reduce the MVP's sensitivity to the UPR.

These objectives were achieved through utilising the set of statistical methods know as Design of Experiments (DoE).

7.2 Significant MVP System Parameters

In any DoE it is advantageous to determine which factors (system parameters) have a significant influence on the critical responses (in this case VMD and buildup) to investigate with advanced modelling. In this thesis a 2-level fractional factorial was used to determine the significant factors which affected the VMD & buildup responses.

Of the initial 55 identified system parameters, a short list of 16 factors were identified for screening experimentation. The screening DoE results indicated that there were 6 factors & one interaction which had an influence on the VMD and 7 factors which had an influence on the buildup.

The relative influence[1] of the significant factors on the VMD was as follows[2]:

(-)Mass UPR **>** (+)Mass Water **>** (+)Mass LMA **>** (-)Mass Styrene **>** (-)Stirrer Speed **>**
(-)[Mass UPR **×** Mass DETA (Organic)] **>** (-)Mass DETA (Organic)

The relative influence[1] of the significant factors on the buildup was as follows[2]:

(+)Mass Styrene **>** (+)Mass DETA (Organic) **>** (-)Initial Reactor Temp. **>** (-)Mass CHP **>**
(-)Mass Water **>** (+)Stirrer Speed **>** (+)Mass LMA

[1] In coded units.

[2] In parenthesis, (+) indicates an increasing effect with an increase in the factor and (-) indicates a decreasing effect with increase in the factor.

The following list of factors was identified for further modelling and optimisation:

1. (A) Quantity of UPR.
2. (B) Quantity of Styrene.
3. (C) Quantity of Lauryl Methacrylate.
4. (D) Quantity of DETA added to the organic phase.
5. (E) Quantity of water.
6. (F) The Stirrer Speed.
7. (G) The Initial Reactor Temperature.

7.3 Statistical Response Surface Modelling

A D-optimal response surface design assuming a quadratic response was identified as the preferred design for modelling the MVP system's responses. The DoE was applied to the identified 7 significant factors and an additional 2 factors [(H) UPR Acid Value and (J) UPR Viscosity] used to quantify the effect of the UPR.

After the model analysis it was determined that the VMD had a reduced 2-factor interaction response surface as described by equation 5.3[1]:

$$\begin{aligned} VMD = 41.68 - 2.61A - 4.57B + 4.74C - 0.05D + 5.39E - 7.21F - 0.04G + 3.50H \\ +8.03J - 2.15AB + 1.73AC - 0.55AD - 1.09AE - 1.71AG + 3.70AH + 1.79BD \\ -3.30BG - 2.17BH - 1.59CH + 1.24DG - 1.37DH + 1.25DJ - 1.29EG + 1.41EJ \\ -2.03FJ - 1.24GH + 5.15HJ \end{aligned} \tag{5.3}$$

The ANOVA indicated that the VMD model was significant with a high R^2 value (0.940) and high Pred-R^2 value (0.839). The suspected influence of the UPR on the VMD was confirmed by the 49.99% effect contribution of the UPR characteristics & their interactions to the total model variance.

The model describing the buildup was also determined to be a reduced 2-factor interaction response model (equation 5.5) however the highly nonlinear buildup response required a natural logarithmic transformation to fit the data more accurately:

$$\begin{aligned} \ln(Buildup + 0.05) = -1.070 - 0.098A + 1.008B + 0.292C - 0.386D - 0.357E + 0.095F \\ -0.327G + 0.017H - 0.422J + 0.352AE - 0.319BE + 0.522BG + 0.365BH \\ +0.450CD - 0.430CH + 0.305DE + 0.477DH - 0.456EG - 0.322EH \\ +0.305EJ - 0.322FJ + 0.557GH - 0.329GJ \end{aligned} \tag{5.5}$$

The ANOVA indicated that the buildup model was significant with reasonably high R^2 value (0.833) but with not the best Pred-R^2 value (0.654) for prediction of the buildup. This can be attributed to the interval nature of the experimental data. The factor with the greatest effect contribution was (B)

[1] The model is in coded units (-1 to 1) for comparison of the modelled terms.

Mass styrene (26.61%). The UPR in itself had a minimal effect contribution (acid value (H) – 0.01% & viscosity (J), - 5.15%) but with the interaction terms had an effect contribution of 37.56%.

The observations of previous authors on the MVP system (Terblanche, 2002; Gous, 2003; Simpson, 2010) which suggested that the UPR had a significant effect on the MVP system, were confirmed by the model and the high effect contributions, of the UPR characteristics and their interactions, to the models.

7.4 Optimisation & Validation

Utilising the response surface models developed for the MVP system and a DoE approach known as Robust Parameter Design (specifically Propagation of Error) an optimised formulation and process was developed for the MVP system. This optimised MVP system was compared to the standard system over the UPR design space.

The average VMD response over the UPR design space was improved from the standard's average of 44.56µm to the optimised system's average of 47.84µm which was significantly closer to the desired optimal of 47.5µm.

The variation of the VMD due to the UPR over the design space was reduced by over 30%[1] from the standard to optimised MVP system. The propagation of error also indicated that the lower the UPR's acid value the less sensitive the MVP are to variations in the UPR quality and therefore further reduction in the MVP sensitivity should be gained by a lower acid value and a narrower UPR design space.

Validation experiments for the response surface models were conducted on UPR from the model experiments and 2 randomly selected UPR batches. The average prediction error for these 12 verification batches was 2.16µm (5.16%) which is only slightly larger than the repeatability standard deviation of 1.96µm. The small 0.2µm difference in these error estimates indicate that the model is very accurate and well suited for predicting the VMD of a MVP batch within the design space.

7.5 Dimensional Analysis Empirical Equations

The Buckingham-Π method was applied to the MVP system parameters and a dimensionless model (equation 6.5) was developed. The model, equation 6.5, parameters were regressed from the data collected from the RSM DoE experimentation.

$$\left(\frac{\alpha}{D}\right) = 7.77 \times 10^{-5} Re_d^{-8.21\times10^{-4}} We_d^{-0.186} Fr^{-0.298} \left(\frac{\rho_c}{\rho_d}\right)^{-10.39} \left(\frac{\mu_c}{\mu_d}\right)^{-0.331} \phi^{-1.218} \tag{6.5}$$

The model developed was not ideal having a R^2 value of only 0.59 and an average error of 21.25%. It did however perform better than models described in literature (Hopff et. al., 1964; Arai et. al., 1977; Chatzi et. al., 1989) including a simplified version of the model, previously developed by Terblanche

[1] Based upon the coefficient of variation.

(2002)[1] for the MVP system. The next best model was the one developed by Hopff et. al. (1964) with a R^2 value of 0.50 and average error 23.61%. The other models had negative R^2 values and were therefore deemed unsuitable for the MVP system.

7.6 Recommendations for Future Work

On completion of this Thesis the following recommendations can be made regarding future work into modelling and optimisation of the MVP system:

1. Effect of batch size:
   - An investigation should be conducted to determine the effect of the batch size on the MVP system responses and to incorporate any effects in the response surface model.
   - The effect of scale should be incorporated into any further investigation into dimensional analysis empirical modelling.
2. Vesiculation mechanism:
   - An investigation into determining the mechanism of vesicle formation should be conducted to improve the understanding of its influence on various system parameters as well as for optimisation of the vesiculation in the MVP.
   - The mechanisms should take into consideration the variation in the UPR characteristics by determining their influence on the vesicle formation.
3. Phenomenological Modelling:
   - A detailed investigation to develop a deterministic model based upon physical phenomena, mechanisms, and fundamental laws, applicable to the MVP system should be conducted to determine the mathematical relationship between the MVP system and the MVP final characteristics.
   - Develop a model for the Suede MVP system using population balance equations.
4. Improvement in the Dimensional Analysis Model:
   - Investigation into the suitability of more advanced dimensionless models should be conducted to find a model that represents the system with a significantly lower error.

[1] It should be noted that the original model was developed for the MVP produced with a saw-tooth mixer and not a pitched blade turbine as in this thesis.

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Appendix A – Experimental Record Template

Batch Number:

SUEDE MULTI-VESICULATED PARTICLE FORMULATION

Std Number

Chemist:

Date:

NR	Batch	CONSTITUENT	%	QUANTITY GRAMS 5L	QUANTITY Added	Container	Mass C. Before	Mass C. After	Mass Total
		STAGE 2(Pre-dispersion - Inert container)							
1		Unsaturated Polyester Resin							
2		Titanium Dioxide							
3		Styrene							
4		Lauryl Methacrylate							
5		Diethylene Triamine							
		STAGE 1 - Aqueous Phase							
6		Water							
7		PVOH Solution							
8		HEC Solution							
9		Diethylene Triamine							
		STAGE 4 - Catalysis							
10		Water							
11		Ferrous Sulphate							
12		Cumene Hydroperoxide							
		STAGE 7 - Post Treatment							
13		Surfactant							
14		Water							
15		25% Ammonia soln							
16		Water							
17		HASE Thickener							
18		Acticide							
		Total							

Variable Process Parameters

Stirrer Speed Stage 1&3		RPM
Initial Water Temp.		°C
Addition Time		min
Emulsification Time		min
Stationary Period		min
Special		

MSc Experimental Procedure

Date: ______________

Run: SCR -__________ Chemist: ______________

Preparation procedure

Prepare Documentation: _______

Prepare _______ & Print _______ Formula.

Fill In all variable process parameters in the manufacturing manual for the specific run. _______

Weight out the Raw Materials the day before the batch isto be made. _______

Weigh the Raw Materials according to the attached Formula filling in all required information.

____

All containers are to be labelled with the following information: _______

Addition Number (NR)
Chemical Name
Raw Material Batch
Batch Run Number
Stage Number

e.g. 3 – Styrene: A
Run: SCR-006
Stage: 1

Store containers and Raw Materials correctly. E.g. Styrene is to be kept in the fridge. _______

Calculate the Theoretical Holdup (ϕ) _______

Hold-up:	Theoretical

Manufacturing Procedure

Batch Number: _______

Staggered Order: 1st 2nd 3rd 4th

Chemist: _______________

Special Treatments of the Procedure (Formula):____
____
____
____

Notes to the Chemist:

The following is a detailed plan of how the MVP are tobe manufactured.

Before starting the batch ensure that the formula specified process parameters have been filled in the manufacturing procedure.

Note any interesting observations such as:

- Viscosity build-up
- Colour changes
- Requirements in speed changes of the stirrer during temperature ramping.
- Etc.

The manufacturing procedure includes all tests to be conducted during the manufacture of the MVP.

PLEASE indicate if any deviations occurred from this plansince it is better to repeat a run than to have erroneous results.

Stage 1 - Aqueous phase:

Charge item 8 - POLYVINYL ALCOHOL SOLUTION to a _______ Lbucket. _______

Charge item 7 - HYDROXYETHYL CELLULOSE SOLUTION the _______L bucket. _______

Charge item 6 – DE-IONISED WATER to the_____L bucket. _______

Mix the contents of the bucket until homogeneous. _______

Add item 9 - DIETHYLENE TRIAMINE slowly. _______

Stir for 5 minutes. (Add simultaneously with Stage 2 –Step 7) _______

Measure the Rheology Curve, Density and Interfacial Tension. _______

Rheology Curve	cP
Specific Gravity	Kg/m^3
Interfacial Tension	mN/m

Add the contents of the bucket to the _______ L reactor vessel. _______

Start the water bath and using the heater and ice get the temperature of the water phase (check with a thermometer) to _______

Temp: Specified	Actual

Start low shear stirrer at Specified rpm. _______

RPM: Specified	Actual

Stage 2 – Organic pre-dispersion:

Ensure water phase is at the correct temperature (Stage 1) before continuing. _______

Charge item 1 - POLYESTER and item 2 - TITANIUM DIOXIDE in a separate ______ L inert container. _______

Disperse at ____ rpm under high shear Cowles (_______ mm blade) disperser for 10 minutes. ____

Reduce speed to ______ rpm and add item 3 - STYRENE slowly and stir for 2 minutes. _______

Charge item 4 – LAURYL METHACRYLATE to vessel. _______

After 2 minutes add item 5 – DIETHYLENE TRIAMINE. (add simultaneously with Stage 2 – Step 11) _______

Stir for at least 5 minutes. _______

Measure the Rheology Curve, Density and Interfacial Tension. _______

Rheology Curve	cP
Specific Gravity	Kg/m^3
Interfacial Tension	mN/m

Stage 3 – Addition and Emulsification:

Record Time from DETA addition to start of stage addition – Should be approximately 10 minutes. _______

Time:

Decant the organic phase into the glass feed vessel and set the pump to the required flow rate.

Add Stage 2 to Stage 1 slowly over a _______ minute period of time _______

RPM: Specified	Actual

During the addition thoroughly clean the Cowles equipment ________

Allow emulsification of _______ minute time period. ________

Thoroughly clean the glass feed vessel and the piping during the emulsification period. ________

START STAGGERED BATCH NOW.

Stage 4 – Initiation:

Premix item 10 - DE-IONISED WATER and item 11 -FERROUS SULPHATE and add to the reactor.

____

Stir for 3 minutes at a pre specified rpm. ________

RPM: Specified	Actual

Charge item 12 - CUMENE HYDROPEROXIDE slowly to the reactor. ________

Stir for 3 minutes. ________

Reduce Speed to ______rpm ________

Observations:

Stage 5 – Curing:

Slowly increase the reactor temperature to 50°C over 30 minutes using a water bath. ________

Time:

Keep temperature at 50°C for 60 minutes. ________

Note any Changes in Stirrer speed as required.

Speed:

Observations:

Stage 6 – Temperature Ramp:

Raise temperature slowly to 60°C over 30 minutes. _______

Time:	Speed:

Keep at 60°C for 3 hours. _______

Note if an excessive amount of product accumulates onthe wall of the reactor. _______

Speed:

Observations:

Switch off the water bath and allow to cool slowly toambient temperature overnight under constant stirring. _______

Post treatment Procedure

Batch Number: _______

Chemist: ______________

Special Treatments of the Procedure (Formula): ____

____

____

____

Notes to the Chemist:

Reuse the buckets that the aqueous phase was prepared in ensuring that it has been thoroughly cleaned and dried.

Clean the reactor thoroughly after decanting.

Please note for cleaning **no soap** is to be used only water. Please also **only** use the designated cleaning equipment for the project.

Post Treatment is to be done using the Cowles (Blade = _______ mm) at _______ rpm.

Please note that only one Cowles machine is to be used ata time since to avoid conflict with the preparation of the next set of batches.

Stage 7 – Post treatment

Stop the stirrer. _______

Decant the reactor contents into a _____ L plastic bucket. _______

Thoroughly clean the reactor and stirrer. _______

Place the _____ L bucket under the Cowles and start mixing at _______ rpm. _______

At ambient temperature, add item 13 - SURFACTANT to the bucket. _______

Mix for **10 minutes**. _______

Slowly add a premix of item 14 – DE-IONISED WATER and item 15 – 25% AMMONIA SOLUTION to the bucket. _______

Mix for **10 minutes**. _______

Stop the Cowles blade and test the pH. _______

pH:

Note: If the pH of the batch is below 8.0, contact Factory Chemist. _______

Very slowly add a premix of item 16 – DE-IONISED WATER and item 17 – HASE THICKENER to the bucket. _______

Stir for **10 minutes**. _______

Add item 18 – ACTICIDE and mix for **10 minutes**. _______

Remove the batch from the Cowles and label accordingly in preparation for testing. _______

Finished Product Test Procedure

The following is a list of the testing to be preformed onthe finished MVP batch. It includes the required time frames etc.

Test	**Time frame**	**Equipment**	**Result**	**Chemist**
SG	Max. 48hrs	SG Cup		
NVC%	Max 48hrs	Moisture		
		Analyzer		
PS	NA	HELOS	APSN	
			APSV	
Brookfield Viscosity	1hr – 24hrs	Brookfield Viscometer	1hr	
Rheology Flow curves	1hr	Paar Physica		
Drawdown	Max. 24hrs	Drawdown Bar	200µm	
CR	24hrs after Drawdown	Coloreye		
pH	1hr	pH Meter	pH	

N	rpm	D	
ϕ		σ	$mN.m^{-1}$
μ_d	$kg.m^{-1}.s^{-1}$ (Pa.s)	μ_c	$kg.m^{-1}.s^{-1}$ (Pa.s)
ρ_d	$kg.m^{-3}$	ρ_c	$kg.m^{-3}$
Re		We	
Fr			

Appendix B: Unsaturated Polyester Resin Lab Synthes is

Figure B.1: UPR Lab Setup

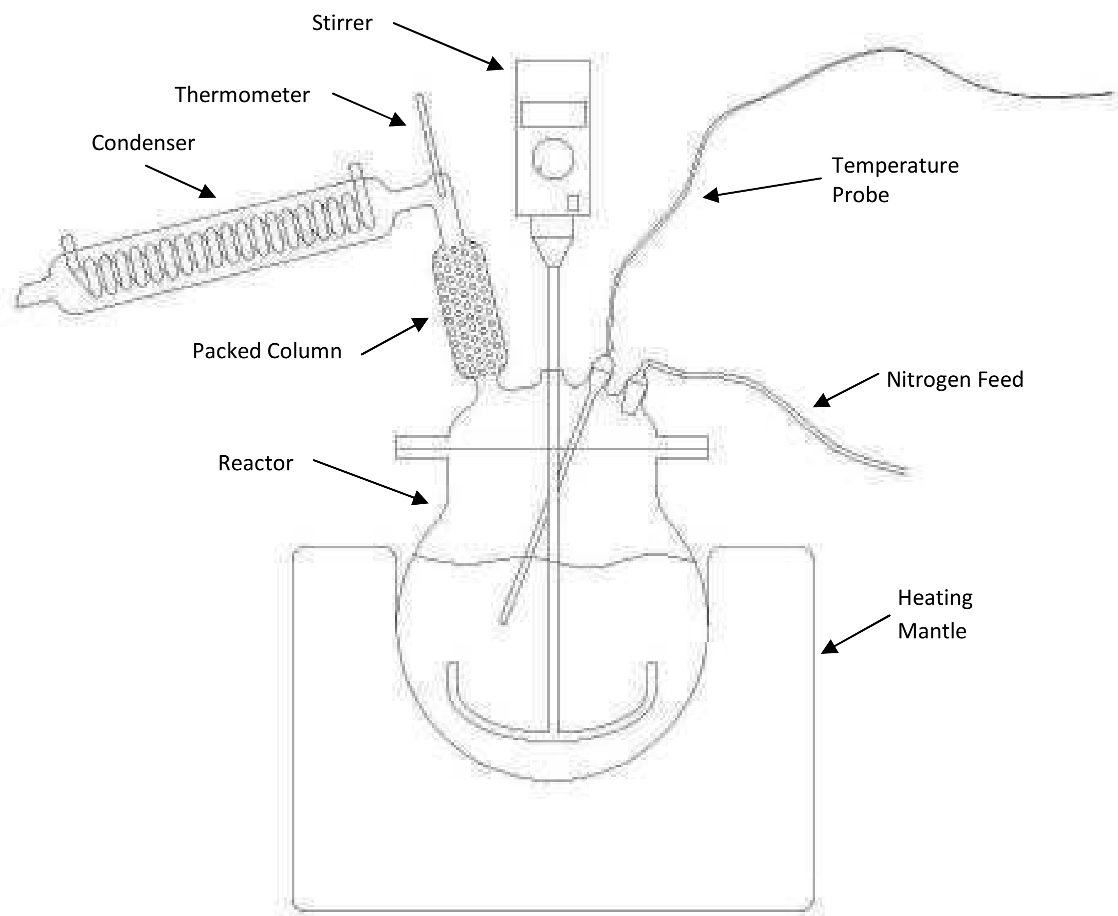


Table B.1: Standard UPR Formulation

Propylene glycol	30.35%
Phthalic anhydride	12.96%
Maleic anhydride	25.75%
Styrene	30.75%
Inhibitor (10% Soln.)	0.18%

Brief description of the UPR lab synthesis process:

1. Nitrogen gas is continuously blown through the glassreactor to remove oxygen from the vessels throughout the process.

2. The propylene glycol, phthalic anhydride and maleic anhydride are charged at room temperature to the vessel and heated to 120°C.

3. The natural exotherm of the mixture raises the temperature of the product to approximately 175°C. The product is then allowed to cool to 160°C.

4. The temperature of the reactor is then increased to between 220 - 260°C depending on the required product specifications.

5. The reaction is allowed to continue whilst the water is drawn off the top of the packed column and condensed. The propylene glycol is condensed in the packed column and flows back to the reactor.

6. The acid value (*ASTM* D1639-90, 1996) and viscosity (*ASTM D1545*, 1998) of the polyester is measured at specified intervals until the required product specifications are met.

7. If the temperature of the top of the packed column falls below 70°C (i.e. water is no longer removed) vacuum can be applied in 1 minute intervals to aid in the water removal and reduction in the aid value.

8. Once the required acid value and viscosity are achieved, heating is removed and the reactor is allowed to cool.

9. The inhibitor and styrene are mixed and placed in an extenally water cooled vessel.

10. Once the UPR's temperature reaches 160°C it is slowly decanted into the styrene. The temperature is continually monitored to ensure that the UPR-styrene mixture never exceeds 60°C.

Appendix C: Screening Experimental Phase Appendices

Appendix C.1: List of Variable Factors

Table C.1: Formulation Factors

Section	Factor	Selected for Short List	Category	Justification
Organic Phase	Mass UPR	**Yes**	2	Suspected to have a significant effect but not known too.
	Batch UPR	No	1	Known to have a significant effect and therefore does not need to be investigated
	Mass TiO_2	**Yes**	3	Suspected not to have a significant effect.
	Mass Styrene	**Yes**	2	Suspected to have a significant effect but not known too.
	Mass LMA	**Yes**	2	Suspected to have a significant effect but not known too.
	Mass DETA	**Yes**	2	Suspected to have a significant effect but not known too.
Aqueous Phase	Mass Water	**Yes**	2	Suspected to have a significant effect but not known too.
	Mass PVOH	**Yes**	2	Suspected to have a significant effect but not known too.
	Grade PVOH	No	2	Beyond the scope of the thesis
	Mass HEC	**Yes**	2	Suspected to have a significant effect but not known too.
	Grade HEC	No	2	Beyond the scope of the thesis
	Mass DETA	**Yes**	3	Suspected not to have a significant effect.
Initiator System	Mass Ferrous Sulphate	**Yes**	3	Suspected not to have a significant effect.
	Mass CHP	**Yes**	3	Suspected not to have a significant effect.
Post Treatment	Mass Surfactant	No	4	Does not affect the PSD or vesiculation only used to modify the rheological properties.
	Mass Ammonia Solution	No	4	Does not affect the PSD or vesiculation only used to adjust the

Section	**Factor**	**Selected for Short List**	**Category**	**Justification**
				pH.
	Mass Thickener	No	4	Does not affect the PSD or vesiculation only used to modify the rheological properties.
	Mass Acticide	No	4	Does not affect the PSD or vesiculation only used to prevent bacterial growth.
Total Factors	**18**	**11**		

Table C.2: Process Factors

Section	**Factor**	**Selected for Short List**	**Category**	**Justification**
Organic Phase Preparation	Dispersion Speed	No	3	Previously determined to ensure sufficient dispersion of the TiO_2.
	Dispersion Temperature	No	3	Uncontrollable on both lab and industrial scale equipment. It has been determine that as long as it is below a threshold temperature there should be no significant effect on the final product.
	TiO_2 Dispersion Time	No	3	Previously determined to ensure sufficient dispersion of the TiO_2.
	Styrene Dispersion Time	No	4	Mixing time deemed sufficient for homogenous mixing. Increasing time will only increase energy consumption and increase the organic phase temperature.
	LMA Dispersion Time	No	4	Mixing time deemed sufficient for homogenous mixing. Increasing time will only increase energy consumption and increase the organic phase temperature.
	DETA Dispersion Time	No	3	Mixing time deemed sufficient for homogenous mixing. Increasing time will only increase

Section	**Factor**	**Selected for Short List**	**Category**	**Justification**
				energy consumption and increase the organic phase temperature.
	Final pH	No	3	Determined by acid number, quantity of polyester and quantity of DETA.
Aqueous Phase Preparation	Initial Reactor Temperature	**Yes**	2	Believed to affect formation of vesicles in droplets.
	Mixing Speed	**Yes**	1	Believed to affect PSD.
	Aeration	No	3	Uncontrolled. Affected by both mixing speed and total volume of the aqueous phase.
	pH of Phase	No	3	Determined by formulation composition.
Addition and Emulsification	Temperature	**Yes**	2	Initial temperature only (see above). Temperature profile is to be monitored.
	Addition rate	**Yes**	2	Determined by addition period and organic phase mass.
	Addition time period	**Yes**	2	Used as primary measure of addition due to its direct (ease) of scale-up to the industrial reactor.
	Mixing Speed during addition	**Yes**	1	Kept the same as above.
	Reactor Hold-up	No	2	Determined by formulation.
	Mixing speed during emulsification	**Yes**	1	Kept the same as above.
	Emulsification time period	**Yes**	2	Believed to affect the PSD as it is necessary for the PSD to reach its dynamic steady state.
Initiator Stage	Rate of Ferrous Sulphate solution addition	No	3	Not analyzed. However the rate was slow enough so as not to shock the system.
	Mixing time before CHP addition	No	3	Previously determined period used since sufficient mixing was achieved.

Section	**Factor**	**Selected for Short List**	**Category**	**Justification**
	CHP addition rate	No	3	Not analyzed. However the rate was slow enough so as not to shock the system.
	CHP mixing period	No	3	Previously determined period used since sufficient mixing was achieved.
	Stationary Stirrer period	**Yes**	2	Droplets may destabilize during this period and start agglomerating or either it allows the particles to stabilize and breakage of the particles is stopped.
Heating phase 1	Stirrer speed	No	3	Particles have started to stabilize and the low shear mixing is only required to aid heat transfer.
	Max temp	No	3	Beyond scope of the thesis.
	Temp change gradient	No	3	Beyond scope of the thesis
	Time period reactor held at max temp.	No	4	Beyond scope of the thesis
Heating phase 2	Stirrer speed	No	3	Speed determined by viscosity and build-up of reactor contents.
	Max temp	No	3	Beyond scope of the thesis
	Temp change gradient	No	4	Beyond scope of the thesis
	Time period reactor held at max temp.	No	4	Beyond scope of the thesis
	Rate of Cooling	No	4	Done as fast as possible. Limited by equipment capabilities.
Post Treatment	Temperature during PT	No	4	A maximum temperature is known below which there should be no significant affect on the product.
	Addition speed of raw materials	No	3	Beyond the scope of thesis. Should have no significant affect at current specification region.

Section	**Factor**	**Selected for Short List**	**Category**	**Justification**
	Mixing time between raw material additions	No	3	Beyond the scope of thesis. Should have no significant affect at current specification region.
	Mixing Speed	No	3	Beyond the scope of thesis. Should have no significant affect at current specification region.
	Final pH	No	3	Adjusted by ammonia addition. The requirement is a pH above 8.0.
Totals	**37**	**5 (8)**		

Appendix C.2: Determination of the Identification Point

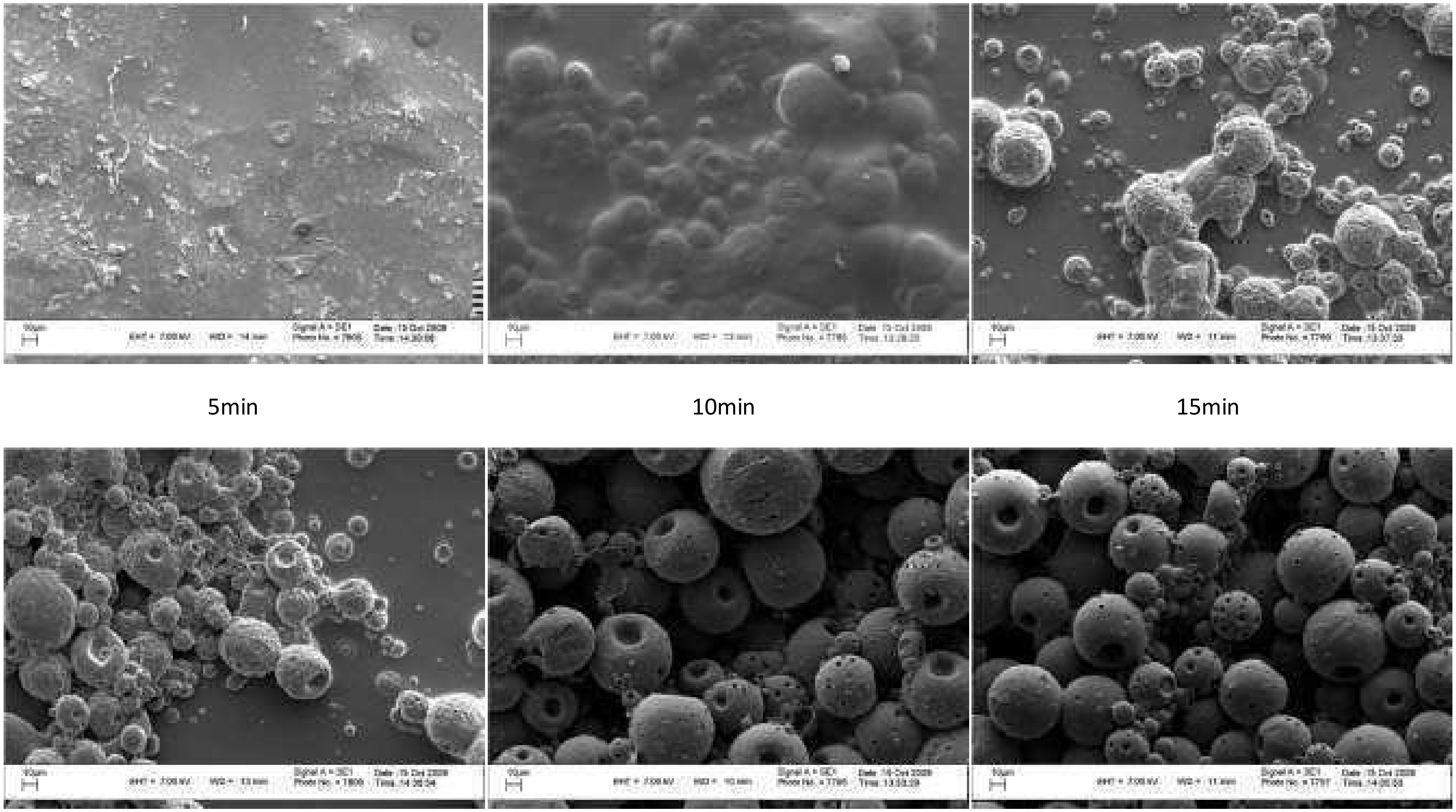
Justification

An investigation was conducted to determine when the during the MVP process, the particle identification point is reached. At this point the particles no longer coalesce or break apart and therefore any experimental variables from this point forward will not influence the PSD. Since the PSD is the main focus of the experimentation any variables after the particle identification point will not need to be considered during any of the screening or modelling experiments.

Experimentation

A standard batch of Suede MVP was manufactured under the standard conditions using the same raw materials as used during the screening phase experiments. At specified time intervals after catalysis a 30ml sample of MVP was taken and quenched with 1ml of a 1% ($^{w}/_{w}$) Potassium Permanganate solution and 19ml of a 5% ($^{w}/_{w}$) Hydroquinone solution. A drawdown of each sample was then taken and the particle formation was observed using a scanning electron microscope (SEM). This work was previously done on the MVP for an older generation product by Terblanche (2002).

Figure C.1: SEM Images of curing MVP at specified time intervals.



5min 10min 15min

20min 30min 40min

50min

60min

90min

Results

Figure C.1 illustrates the following:

5min: No particle formation has occurred. Slight curing has occurred but the organic phase appears as bits rather than round particles.

10min: Particles begin to form but are not distinct yet.

15min: Particles begin to separate but are still soft. The outer-shell of the particles has not formed yet.

20min: Particles are beginning to become spherical in shape but the outer-shell has not formed yet and the particle surface is still very irregular.

30min: Outer-shell has formed, particles are now distinct but still soft (top centre of image) and easily deformed. **(Particle Identification Point)**

40min: Particles have formed and are stable but still soft.

50min: Particles are stable but are still soft.

60min: Particles are distinct and no longer soft.

90min: Particles do not differ from particles at 60min.

From figure C.1 it can be seen that the particles' outer-shell has formed by 30 minutes. Although the particles are still soft at 30minutes it is safe to assume that the particle size distribution (PSD) has stabilized and that at this point the particle identification point has been reached.

After initial catalysis the stirrer is stopped for 30minutes before the heating stages begin (Standard Process) Since the suspension is not heated for 30minutes after catalysis it is safe to assume that the heating of the suspension has no significant effect on the particle size distribution.

This however does not validate any assumption that the opacity is not affected by the heating of the suspension since the particles are still soft and therefore the vesicles could vary depending on the heating of the product as they are not yet stable (particle is still soft at this stage). This is however is beyond the scope of the thesis.

Appendix C.3: Screening Phase Design, Results & Diagnostics

Table C.3: Uncoded Factor Levels for the Screening Design

Coded Factor in DX7®		A	B	C	D	E	F	G	H	J	K	L	M	N	O	P	Q
Run Number:	Std No:	Mass Polyester	Mass TiO_2	Mass Styrene	Mass LMA	Mass DETA (Organic)	Mass Water	Mass PVOH Soln.	Mass HEC Soln.	Mass DETA (Aqueous)	Mass $FeSO_4$	Mass CHP	Initial Reactor Temperature	Stirrer Speed	Addition Rate	Emulsification Time	Stationary Period
SCR-001	13	651.02g	31.68g	319.45g	37.03g	8.06g	2608 .31g	690.62g	444.96g	2.15g	0.38g	6.91g	30°C	330rpm	1 5min	10min	0min
SCR-002	31	651.02g	52.80g	319.45g	37.03g	12.10g	231 3.03g	565.06g	444.96g	3.23g	0.38g	4.61g	30°C	270rpm	15min	30min	0min
SCR-003	18	795.70g	31.68g	236.11g	24.69g	12.10g	260 8.31g	690.62g	543.84g	2.15g	0.38g	4.61g	30°C	270rpm	15min	30min	0min
SCR-004	33	723.36g	42.24g	277.78g	30.86g	10.08g	246 0.67g	627.84g	494.40g	2.69g	0.48g	5.76g	22.5°C	300r pm	10min	20min	20min
SCR-005	1	651.02g	31.68g	236.11g	24.69g	8.06g	2313.03g	565.06g	444.96g	2.15g	0.38g	4.61g	15°C	270rpm	5min	1 0min	0min
SCR-006	22	795.70g	31.68g	319.45g	24.69g	12.10g	2313.03g	690.62g	444.96g	3.23g	0.38g	6.91g	15°C	270rpm	15min	10min	40min
SCR-007	35	723.36g	42.24g	277.78g	30.86g	10.08g	246 0.67g	627.84g	494.40g	2.69g	0.48g	5.76g	22.5°C	300r pm	10min	20min	20min
SCR-008	7	651.02g	52.80g	319.45g	24.69g	8.06g	2313.03g	690.62g	543.84g	2.15g	0.58g	6.91g	15 °C	270rpm	15min	30min	0min
SCR-009	2	795.70g	31.68g	236.11g	24.69g	8.06g	2608.31g	690.62g	543.84g	2.15g	0.58g	6.91g	15°C	330rpm	5min	10min	40min
SCR-010	32	795.70g	52.80g	319.45g	37.03g	12.10g	2608.31g	690.62g	543.84g	3.23g	0.58g	6.91g	30°C	330rpm	15min	30min	40min
SCR-011	4	795.70g	52.80g	236.11g	24.69g	8.06g	2313.03g	565.06g	543.84 g	3.23g	0.38g	6.91g	30°C	330rpm	15min	10min	0min
SCR-012	26	795.70g	31.68g	236.11g	37.03g	12.10g	2608.31g	565.06g	444.9 6g	3.23g	0.38g	4.61g	30°C	330rpm	5min	10min	40min
SCR-013	36	723.36g	42.24g	277.78g	30.86g	10.08g	246 0.67g	627.84g	494.40g	2.69g	0.48g	5.76g	22.5°C	300r pm	10min	20min	20min
SCR-014	34	723.36g	42.24g	277.78g	30.86g	10.08g	246 0.67g	627.84g	494.40g	2.69g	0.48g	5.76g	22.5°C	300r pm	10min	20min	20min
SCR-015	5	651.02g	31.68g	319.45g	24.69g	8.06g	2608. 31g	565.06g	543.84g	3.23g	0.38g	6.91g	30°C	270rpm	5m in	30min	40min
SCR-016	28	795.70g	52.80g	236.11g	37.03g	12.10g	231 3.03g	690.62g	444.96g	2.15g	0.58g	4.61g	15°C	330rpm	15min	10min	0min
SCR-017	37	723.36g	42.24g	277.78g	30.86g	10.08g	246 0.67g	627.84g	494.40g	2.69g	0.48g	5.76g	22.5°C	300r pm	10min	20min	20min
SCR-018	17	651.02g	31.68g	236.11g	24.69g	12.10g	2313.03g	565.06g	444.96g	2.15g	0.58g	6.91g	30°C	330 rpm	15min	30min	40min
SCR-019	19	651.02g	52.80g	236.11g	24.69g	12.10g	2608.31g	690.62g	444.96g	3.23g	0.38g	6.91g	15°C	330rpm	5min	3 0min	0min
SCR-020	3	651.02g	52.80g	236.11g	24.69g	8.06g	2608.31g	690.62g	444.96g	3.23g	0.58g	4.61g	30°C	270rpm	15min	10min	40min
SCR-021	29	651.02g	31.68g	319.45g	37.03g	12.10g	260 8.31g	690.62g	444.96g	2.15g	0.58g	4.61g	15°C	270rpm	5min	30min	40min
SCR-022	6	795.70g	31.68g	319.45g	24.69g	8.06g	2313.03g	690.62g	444.96g	3.23g	0.58g	4.61g	30°C	330rpm	5min	30min	0min
SCR-023	21	651.02g	31.68g	319.45g	24.69g	12.10g	2608.31g	565.06g	543.84g	3.23g	0.58g	4.61g	15°C	330rpm	15min	10min	0min

Coded Factor in DX7®		A	B	C	D	E	F	G	H	J	K	L	M	N	O	P	Q
Run Number:	Std No:	Mass Polyester	Mass TiO_2	Mass Styrene	Mass LMA	Mass DETA (Organic)	Mass Water	Mass PVOH Soln.	Mass HEC Soln.	Mass DETA (Aqueous)	Mass $FeSO_4$	Mass CHP	Initial Reactor Temperature	Stirrer Speed	Addition Rate	Emulsification Time	Stationary Period
SCR-024	12	795.70g	52.80g	236.11g	37.03g	8.06g	2313 .03g	690.62g	444.96g	2.15g	0.38g	6.91g	30°C	270rpm	5min	3 0min	40min
SCR-025	15	651.02g	52.80g	319.45g	37.03g	8.06g	2313 .03g	565.06g	444.96g	3.23g	0.58g	6.91g	15°C	330rpm	5min	10min	40min
SCR-026	25	651.02g	31.68g	236.11g	37.03g	12.10g	2313.03g	690.62g	543.84g	3.23g	0.58g	6.91g	30°C	270rpm	5min	10min	0min
SCR-027	24	795.70g	52.80g	319.45g	24.69g	12.10g	2608.31g	565.06g	444.96g	2.15g	0.58g	6.91g	30°C	270rpm	5min	10min	0min
SCR-028	11	651.02g	52.80g	236.11g	37.03g	8.06g	2608 .31g	565.06g	543.84g	2.15g	0.58g	4.61g	30°C	330rpm	5min	30min	0min
SCR-029	16	795.70g	52.80g	319.45g	37.03g	8.06g	2608.31g	690.62g	543.84g	3.23g	0.38g	4.61g	15°C	270rpm	5min	10min	0min
SCR-030	23	651.02g	52.80g	319.45g	24.69g	12.10g	2313.03g	690.62g	543.84g	2.15g	0.38g	4.61g	30°C	330rpm	5min	10min	40min
SCR-031	14	795.70g	31.68g	319.45g	37.03g	8.06g	2313.03g	565.06g	543.84g	2.15g	0.58g	4.61g	30°C	270rpm	15min	10min	40min
SCR-032	30	795.70g	31.68g	319.45g	37.03g	12.10g	2313.03g	565.06g	543.84g	2.15g	0.38g	6.91g	15°C	330rpm	5min	3 0min	0min
SCR-033	27	651.02g	52.80g	236.11g	37.03g	12.10g	2608.31g	565.06g	543.84g	2.15g	0.38g	6.91g	15°C	270 rpm	15min	10min	40min
SCR-034	9	651.02g	31.68g	236.11g	37.03g	8.06g	2313. 03g	690.62g	543.84g	3.23g	0.38g	4.61g	15°C	330rpm	15 min	30min	40min
SCR-035	10	795.70g	31.68g	236.11g	37.03	8.06g	2608. 31g	565.06g	444.96g	3.23g	0.58g	6.91g	15°C	270rpm	15min	30min	0min
SCR-036	8	795.70g	52.80g	319.45g	24.69g	8.06g	2608. 31g	565.06g	444.96g	2.15g	0.38g	4.61g	15°C	330rpm	15min	30min	40min
SCR-037	20	795.70g	52.80g	236.11g	24.69g	12.10g	231 3.03g	565.06g	543.84g	3.23g	0.58g	4.61g	15°C	270rpm	5min	30min	40min

Table C.4: Response Results for the Screening Design

Run Number:	Buildup	SG	NVC%	SMD	VMD	SDevS	SDevV	Brookfield Viscosity	Contrast Ratio	CV (SMD)	CV (VMD)	Coarseness	Tint Strength (ave)
SCR-001	1	1.0352	24.18%	22.43μm	43.71μm	21.85μm	22. 29μm	2799cP	67.75%	97.41%	51.00%	4	74.15%
SCR-002	5	1.0262	26.37%	19.17μm	56.52μm	26.72μm	31. 38μm	10878cP	77.35%	139.38%	55.52%	5	75.52%
SCR-003	0	1.0462	24.08%	19.79μm	36.31μm	18.30μm	17. 74μm	859.8cP	37.54%	92.47%	48.86%	2	72.78%
SCR-004	1	1.0484	25.20%	22.01μm	41.31μm	20.61μm	21. 26μm	3579cP	85.06%	93.64%	51.46%	2	76.39%
SCR-005	0	1.0480	25.88%	39.53μm	55.37μm	25.03μm	25. 52μm	1900cP	82.12%	63.32%	46.09%	4	75.05%
SCR-006	5	1.0500	26.86%	6.42μm	11.13μm	5.49μm	6.26μ m	9498cP	96.98%	85.51%	56.24%	0	73.93%
SCR-007	2	1.0458	25.32%	24.20μm	44.93μm	22.40μm	22. 71μm	4119cP	79.32%	92.56%	50.55%	2	74.02%
SCR-008	1	1.0492	24.75%	17.02μm	28.12μm	13.75μm	13. 92μm	2719cP	86.02%	80.79%	49.50%	1	80.49%
SCR-009	0	1.0470	23.79%	21.31μm	35.41μm	17.33μm	16. 39μm	659.3cP	66.82%	81.32%	46.29%	2	77.28%
SCR-010	3	1.0311	25.94%	14.19μm	30.73μm	15.32μm	18. 72μm	5499cP	65.22%	107.96%	60.92%	1	73.23%
SCR-011	0	1.0375	26.09%	18.84μm	28.45μm	13.45μm	12. 30μm	1320cP	68.64%	71.39%	43.23%	1	79.04%
SCR-012	2	1.0477	25.24%	38.39μm	57.68μm	27.21μm	29. 04μm	4479cP	81.98%	70.88%	50.35%	4	74.93%
SCR-013	1	1.0521	25.33%	24.03μm	43.56μm	21.66μm	21. 70μm	3519cP	82.78%	90.14%	49.82%	3	79.00%
SCR-014	1	1.0485	24.67%	23.57μm	40.61μm	20.04μm	20. 78μm	2919cP	77.92%	85.02%	51.17%	3	75.08%
SCR-015	1	1.0385	23.25%	18.90μm	37.27μm	18.63μm	21. 18μm	999.8cP	36.74%	98.57%	56.83%	2	70.20%
SCR-016	5	1.0324	26.28%	17.85μm	28.98μm	14.10μm	13. 86μm	7538cP	73.37%	78.99%	47.83%	1	83.42%
SCR-017	0	1.0459	24.76%	25.24μm	44.68μm	22.15μm	21. 59μm	2939cP	73.30%	87.76%	48.32%	3	75.85%
SCR-018	1	1.0451	24.38%	18.76μm	39.24μm	19.60μm	22. 20μm	4499cP	70.79%	104.48%	56.57%	3	75.25%
SCR-019	2	1.0394	22.34%	24.24μm	46.37μm	23.16μm	23. 67μm	16649cP	82.08%	95.54%	51.05%	2	69.74%
SCR-020	0	1.0469	22.37%	50.91μm	66.03μm	27.74μm	26. 69μm	659.9cP	49.13%	54.49%	40.42%	4	74.29%
SCR-021	5	1.0299	23.54%	28.49μm	73.13μm	35.66μm	41. 48μm	>EEE	68.43%	125.17%	56.72%	5	62.97%
SCR-022	3	1.0478	26.99%	8.25μm	16.22μm	8.11μm	8.23μ m	1336cP	56.58%	98.30%	50.74%	0	69.96%
SCR-023	5	1.0164	22.96%	25.18μm	61.37μm	30.19μm	34. 66μm	17756cP	78.33%	119.90%	56.48%	5	66.16%
SCR-024	1	1.0543	26.29%	32.07μm	41.02μm	16.94μm	16. 05μm	2048cP	73.85%	52.82%	39.13%	1	77.73%

Run Number:	Buildup	SG	NVC%	SMD	VMD	SDevS	SDevV	Brookfield Viscosity	Contrast Ratio	CV (SMD)	CV (VMD)	Coarseness	Tint Strength (ave)
SCR-025	5	1.0247	26.39%	25.13µm	44.19µm	21.89µm	23. 42µm	6359cP	78.40%	87.11%	53.00%	3	81.35%
SCR-026	1	1.0434	23.65%	37.85µm	71.92µm	35.91µm	37. 04µm	16077cP	79.59%	94.87%	51.50%	5	70.28%
SCR-027	1	1.0541	27.43%	30.87µm	42.29µm	18.77µm	19. 07µm	1632cP	84.87%	60.80%	45.09%	2	82.11%
SCR-028	0	1.0459	22.30%	38.09µm	62.05µm	30.21µm	31. 62µm	1068cP	70.51%	79.31%	50.96%	4	77.72%
SCR-029	3	1.0499	25.84%	33.70µm	44.68µm	19.24µm	19. 20µm	2919cP	83.76%	57.09%	42.97%	3	80.68%
SCR-030	5	1.0362	24.18%	7.49µm	13.53µm	6.72µm	8.21µ m	15737cP	93.73%	89.72%	60.68%	0	66.15%
SCR-031	3	1.0302	26.84%	21.06µm	37.29µm	18.49µm	16. 71µm	1516cP	52.24%	87.80%	44.81%	2	72.25%
SCR-032	5	1.0506	26.79%	7.87µm	14.96µm	7.47µm	9.12µ m	2180cP	93.20%	94.92%	60.96%	0	74.34%
SCR-033	2	1.0437	22.79%	31.51µm	64.04µm	32.02µm	37. 79µm	11877cP	84.35%	101.62%	59.01%	5	69.64%
SCR-034	1	1.0430	23.22%	19.12µm	36.34µm	18.15µm	18. 92µm	4599cP	86.23%	94.93%	52.06%	3	78.60%
SCR-035	0	1.0464	24.05%	40.92µm	62.88µm	29.98µm	32. 68µm	615.9cP	68.89%	73.26%	51.97%	4	75.60%
SCR-036	4	1.0506	25.44%	19.03µm	30.9µm	15.04µm	13.7 5µm	1276cP	81.39%	79.03%	44.47%	1	77.89%
SCR-037	3	1.0522	25.29%	7.99µm	13.6µm	6.71µm	7.35µm	3359cP	94.84%	83.98%	53.96%	1	72.67%

Table C.5: Percentage Effects Contribution* for All Responses

Factor / Response	Mass Polyester	Mass TiO_2	Mass Styrene	Mass LMA	Mass DETA (Organic)	Mass Water	Mass PVOH Soln.	Mass HEC Soln.	Mass DETA (Aqueous)	Mass $FeSO_4$	Mass CHP	Initial Reactor Temperature	Stirrer Speed	Addition Rate	Emulsification Time	Stationary Period	2-factor Interactions	Error
VMD	**22.78%**	0.76%	**8.17%**	**13.93%**	**0.02%**	**21.33%**	2.29%	3.18%	0.49%	2.90%	0.75%	0.26%	**7.35%**	0.02%	2.07%	1.51%	**AE: 4.18%**	8.01%
Buildup	0.23%	1.24%	**34.62%**	**3.06%**	**18.44%**	**5.69%**	0.03%	1.24%	0.63%	0.03%	**5.69%**	**9.13%**	**3.06%**	0.03%	0.23%	2.05%		14.60%
SDevV	**29.52%**	1.99%	**4.14%**	**16.48%**	**1.66%**	**20.23%**	**3.86%**	1.33%	0.69%	**2.94%**	0.17%	0.00%	**4.47%**	0.01%	0.46%	0.87%	**AE: 4.96%**	6.22%
%CV (VMD)	**9.97%**	4.43%	**9.02%**	1.38%	**32.93%**	0.20%	1.54%	5.16%	1.04%	0.01%	2.42%	1.36%	4.04%	0.0 2%	5.75%	2.16%		18.57%
Brookfield Viscosity	**22.03%**	0.01%	1.77%	1.10%	**38.23%**	0.01%	**4.10%**	0.03%	1.74%	0.00%	0.31%	**4.23%**	0.11%	0.52%	1.66%	0.07%	**AE: 13.60%** **EG: 3.02%**	7.46%
SG	**14.27%**	0.08%	**10.23%**	**5.24%**	**2.69%**	0.00%	**0.61%**	**0.33%**	**3.49%**	**3.11%**	**1.74%**	**0.05%**	**6.50%**	**6.67%**	**2.97%**	0.01%	**AC: 10.48%** **AE: 2.82%** **AG: 2.16%** **AH: 3.73%** **AJ: 2.84%** **AM: 3.00%** **AO: 6.57%**	10.41%
NVC%	**38.51%**	0.79%	**15.88%**	0.54%	0.01%	**24.98%**	**2.12%**	**6.15%**	0.17%	0.14%	0.19%	0.47%	0.31%	0.27%	1.35%	0.72%		7.40%
SMD	**5.89%**	0.15%	**18.72%**	**7.06%**	**6.60%**	**19.10%**	1.30%	**5.52%**	0.21%	1.67%	0.54%	**0.82%**	**9.81%**	1.17%	**7.24%**	1.35%	**CM: 4.28%**	8.57%
SDevS	**25.80%**	1.79%	**7.41%**	**15.00%**	**0.08%**	**21.02%**	2.68%	1.77%	0.39%	3.29%	0.36%	0.11%	**5.00%**	0.00%	1.41%	1.56%	**AE: 4.73%**	7.61%
%CV (SMD)	**15.89%**	**6.75%**	**11.83%**	**1.79%**	**21.26%**	0.05%	0.20%	1.25%	1.02%	0.29%	0.18%	0.00%	2.50%	**4.68%**	**10.03%**	0.01%	**AD : 5.13%** **AE : 5.00%**	12.14%
CR	0.06%	6.53%	0.39%	0.64%	**10.14%**	**10.48%**	0.61%	0.11%	0.00%	3.01%	0.58%	**24.49%**	1.46%	2.98%	2.25%	0.04%		36.23%
Coarseness (Paint)	**31.51%**	3.50%	5.04%	**14.01%**	0.14%	**14.01%**	5.04%	1.26%	1.26%	1.26%	2.24%	0.00%	5.04%	0.56%	3.5 0%	1.26%		10.37%
Tint Strength	**10.51%**	**13.95%**	2.13%	1.57%	**14.54%**	**2.95%**	0.82%	2.08%	0.71%	0.09%	2.26%	0.84%	0.70%	1.51%	**1.07%**	3.42%	**AE: 11.73%** **AF: 9.97%** **AP: 7.63%**	21.52%

* The percentage effect contribution is sum of squar es (see ANOVA) of the effect as a percentage of the total sum of squares for all the effects. The perc entage effect contribution is only comparable if the effect terms have the sam e degrees of freedom.

Table C.6 – Regressed Equation Coefficients for All Responses (Coded)

Factor / Response	Intercept	Mass Polyester	Mass TiO_2	Mass Styrene	Mass LMA	Mass DETA (Organic)	Mass Water	Mass PVOH Soln.	Mass HEC Soln.	Mass DETA (Aqueous)	Mass $FeSO_4$	Mass CHP	Initial Reactor Temperature	Stirrer Speed	Addition Rate	Emulsification Time	Stationary Period	2-Factor Interactions
VMD	41.62	-8.33		-4.99	6.51	-0.25	8.06							-4.73				-3.57 AE
Buildup	2.28			1.16	0.34	0.84	-0.47					-0.47	-0.59	0.34				
SDevV	21.14	-5.11		-1.91	3,82	1.21	4.23	-1.85			1.61			-1.99				-2.09 AE
%CV (VMD)	51.10	-1.86		1.77		3.38												
Brookfield Viscosity	5665.96	-2745.02				3616.34		1183.79					-1202.99					-2156.68AE 1016.01EG
SG	1.0419	0.0036		-0.0031	-0.0022	-0.0016		0.0008	-0.0006	-0.0018	-0.0017	0.0013	-0.0002	- 0.002 5	-0.0025	0.0017		0.0031 AC 0.0016 AE 0.0014 AG 0.0019 AH 0.0016 AJ 0.0017 AM 0.0025 AO
NVC%	24.87%	0.96%		0.62%			-0.77%	-0.23%	-0.38%									
SMD	23.82	-2.66		-4.75	2.92	-2.82	4.80		-2.58				0.99	-3.44		-2.96		-2.27 CM
SDevS	19.97	-4.23		-2.27	3.22	0.24	3.82							-1.86				-1.81 AE
%CV (SMD)	87.60	-7.81	-5.10	6.74	2.62	9.04									4.24	6.21		-4.44 AD 4.38 AE
CR	74.11%					4.80%	-4.88%						-7.46%					
Coarseness (Paint)	2.50	-0.94			0.63		0.63											
Tint Strength	74.54%	1.57%	1.81%			-1.85%	-0.83%									-0.50%		-1.66% AE 1.53% AF 1.34% AP

Figure C.2.1: Effect Charts for the VMD (a) Half-Normal Plot (b) Pareto Chart

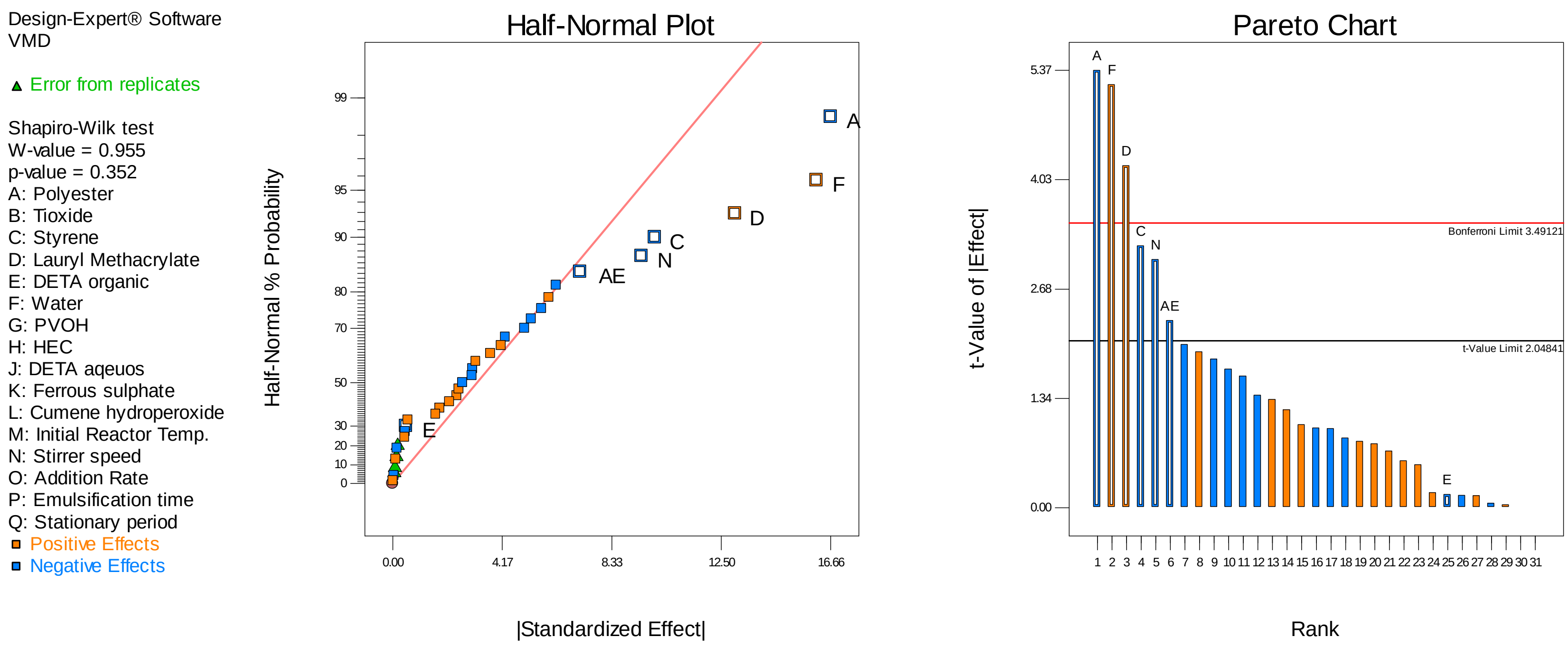
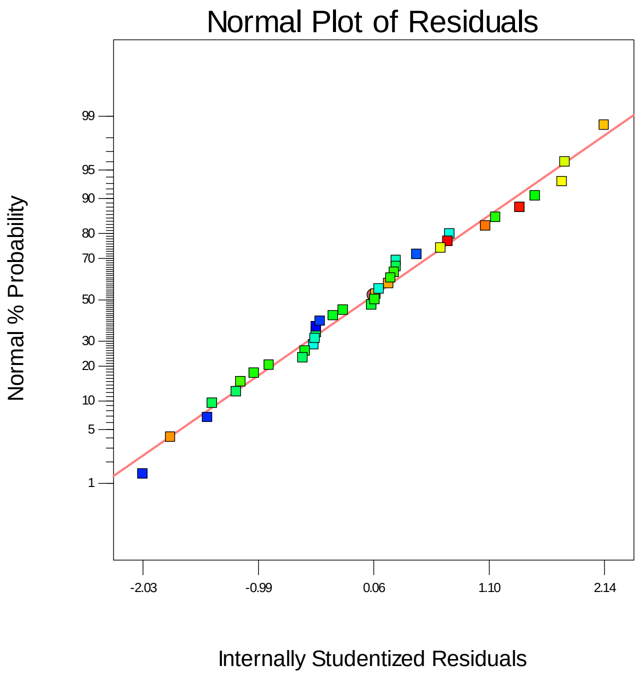
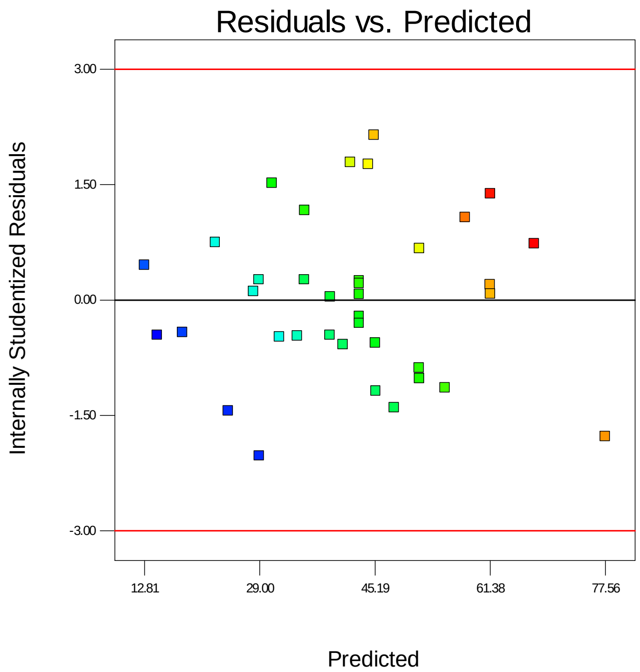


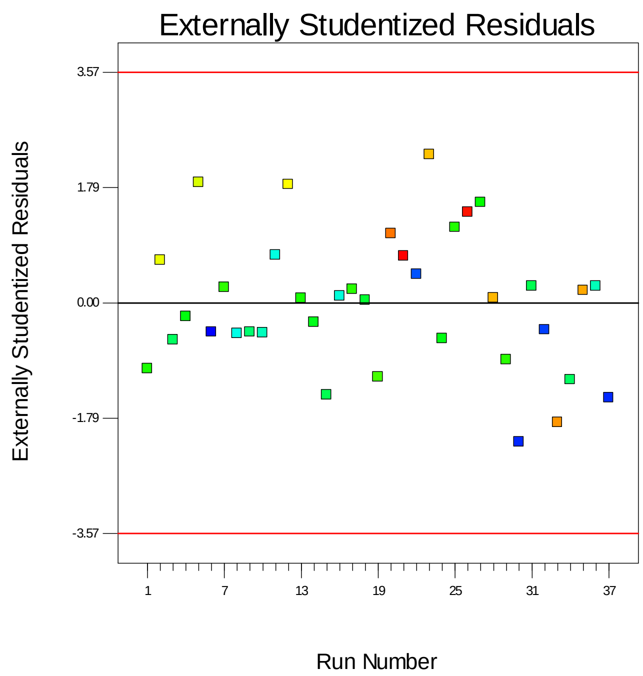
Figure C.2.2: Diagnostic Charts for the VMD (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.

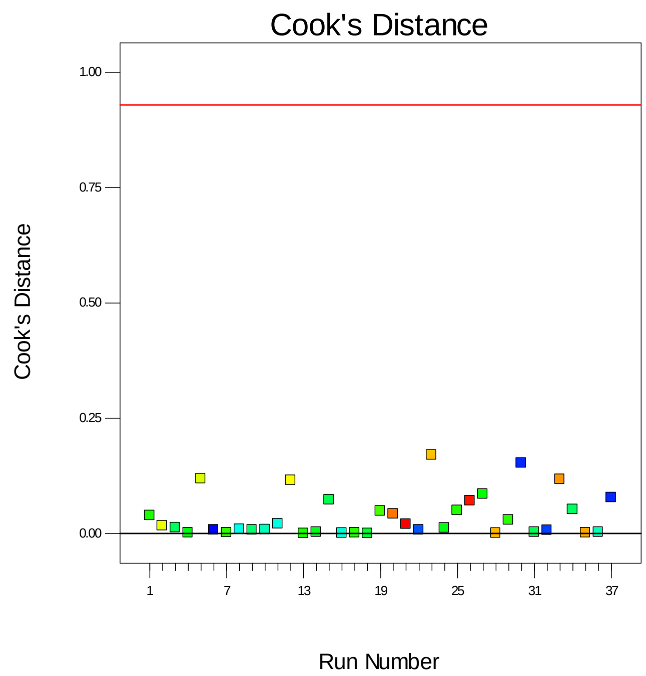


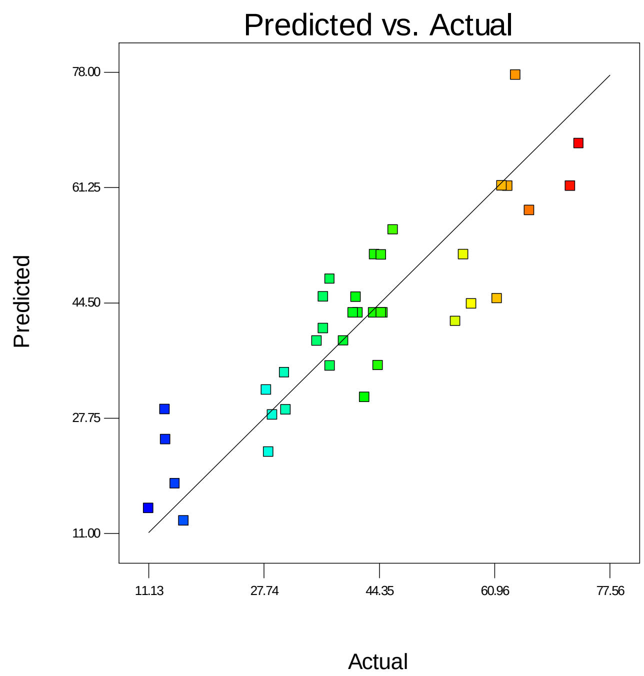
Normal Plot of Residuals
Normal % Probability
99
95
90
80
70
50
30
20
10
5
1
-2.03
-0.99
0.06
1.10
2.14
Internally Studentized Residuals



Residuals vs. Predicted
Internally Studentized Residuals
3.00
1.50
0.00
-1.50
-3.00
12.81
29.00
45.19
61.38
77.56
Predicted


Externally Studentized Residuals
Externally Studentized Residuals
3.57
1.79
0.00
-1.79
-3.57
1
7
13
19
25
31
37
Run Number


Cook's Distance
Cook's Distance
1.00
0.75
0.50
0.25
0.00
1
7
13
19
25
31
37
Run Number



Predicted vs. Actual
Predicted
Actual
78.00
61.25
44.50
27.75
11.00
11.13
27.74
44.35
60.96
77.56

Figure C.3.1: Effect Charts for the Buildup (a) Half-Normal Plot (b) Pareto Chart

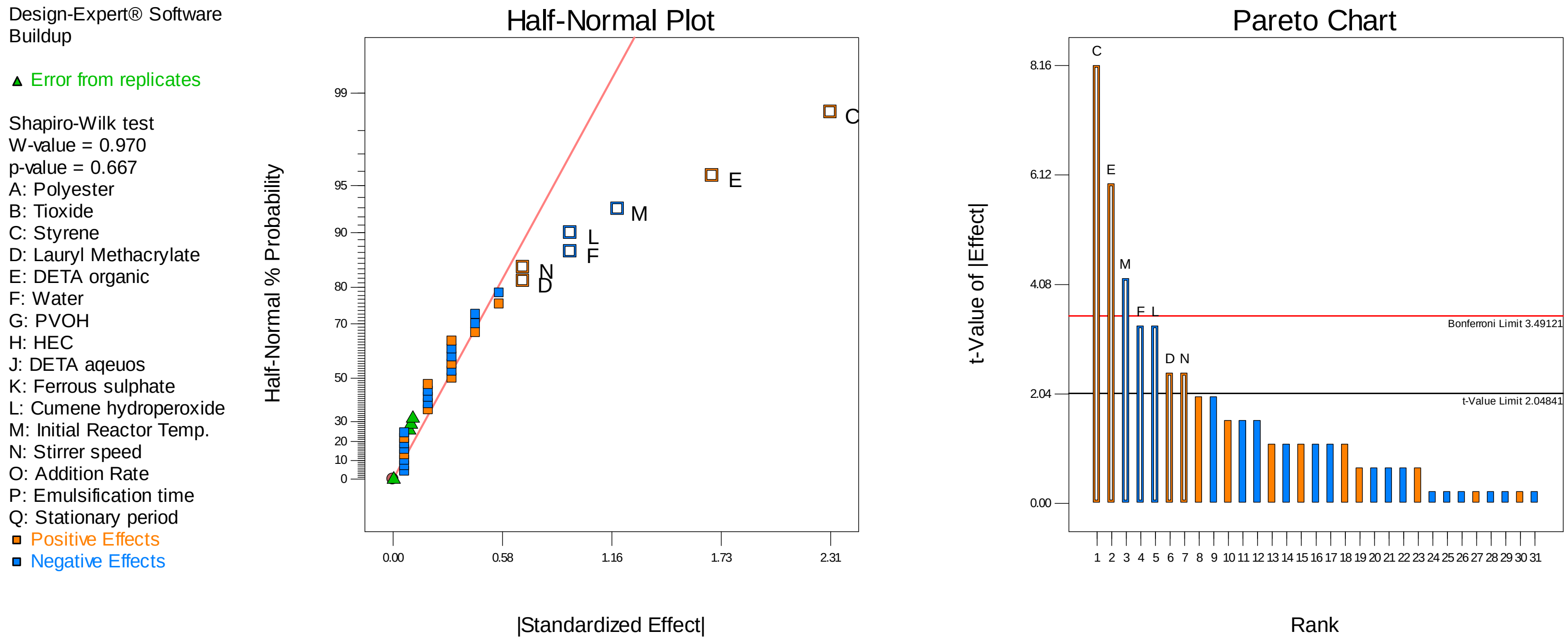
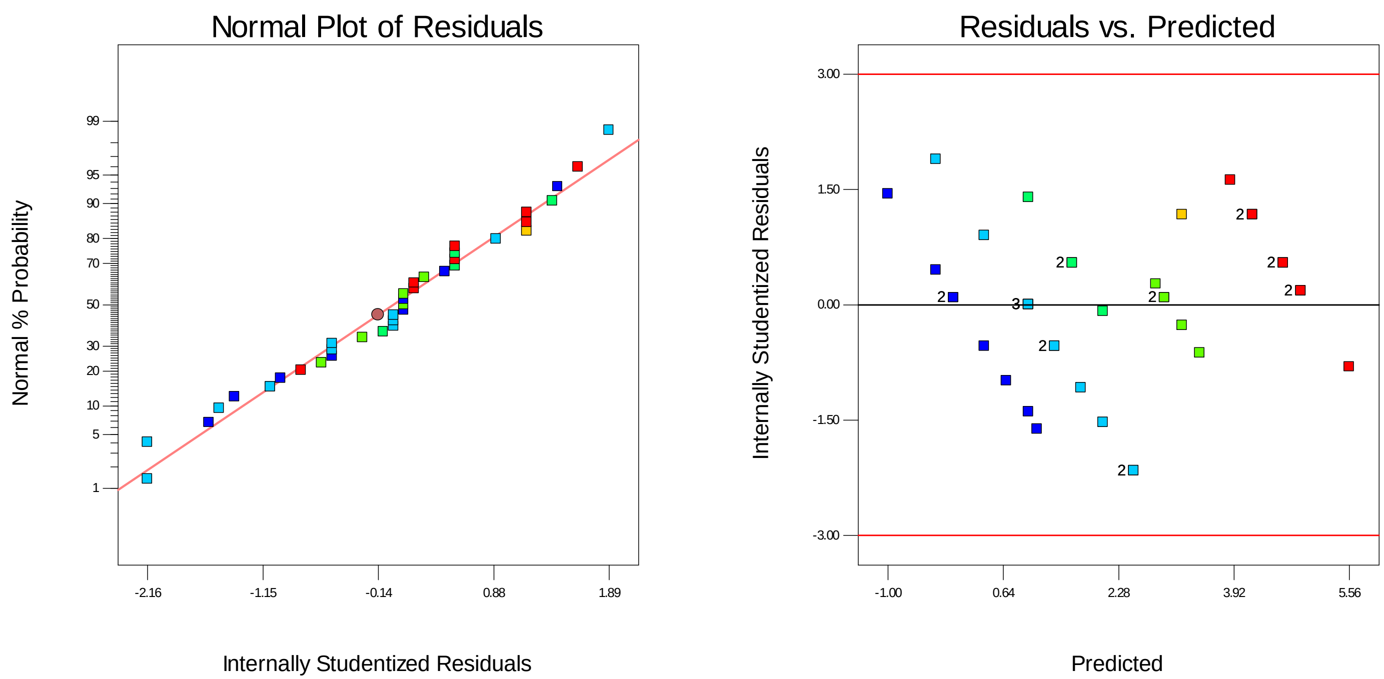
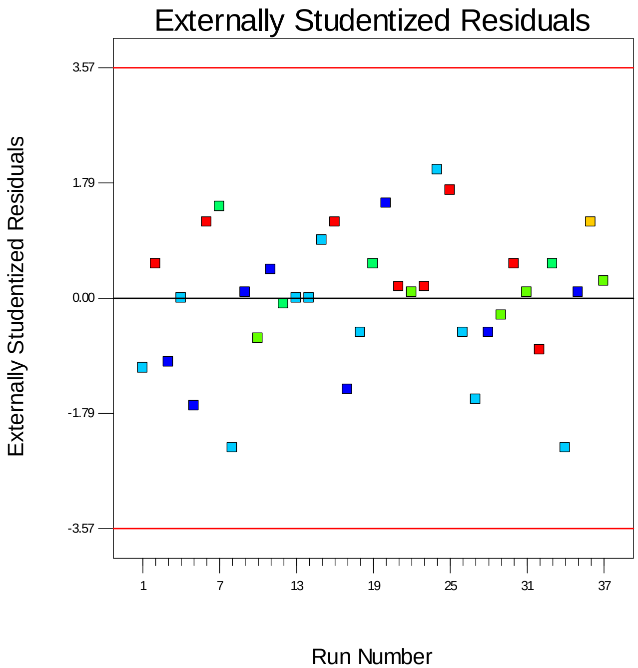
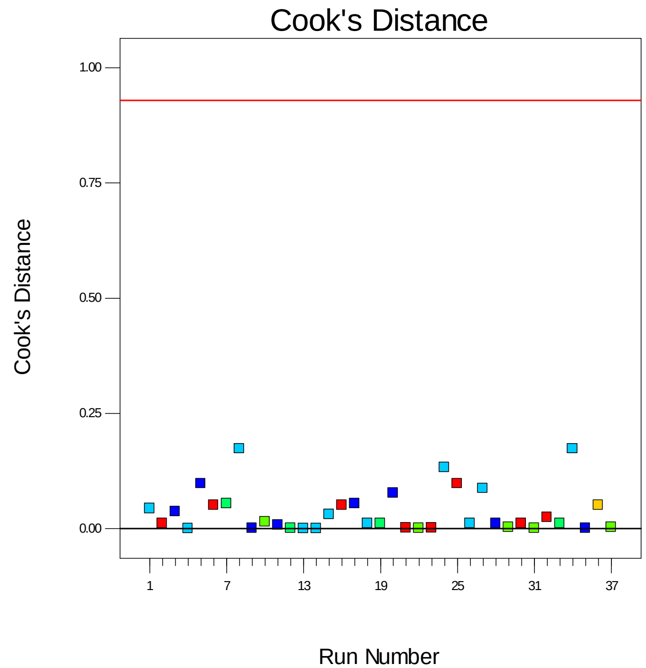


Figure C.3.2: Diagnostic Charts for the VMD (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.





Externally Studentized Residuals
Externally Studentized Residuals
3.57
1.79
0.00
-1.79
-3.57
1
7
13
19
25
31
37
Run Number



Cook's Distance
Cook's Distance
1.00
0.75
0.50
0.25
0.00
1
7
13
19
25
31
37
Run Number

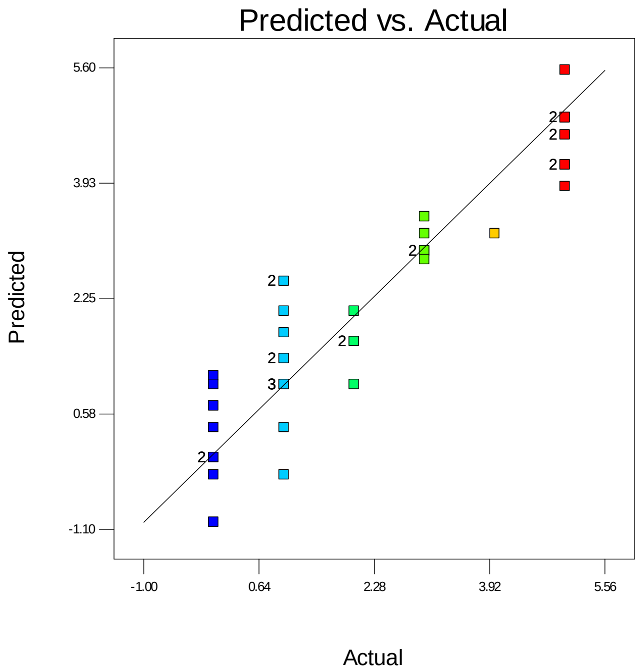

Predicted vs. Actual
5.60
3.93
2.25
0.58
-1.10
Predicted
-1.00
0.64
2.28
3.92
5.56
Actual
2
2
2
2
2
2
2
3
2

Figure C.4.1: Effect Charts for the SDevV (a) Half-Normal Plot (b) Pareto Chart

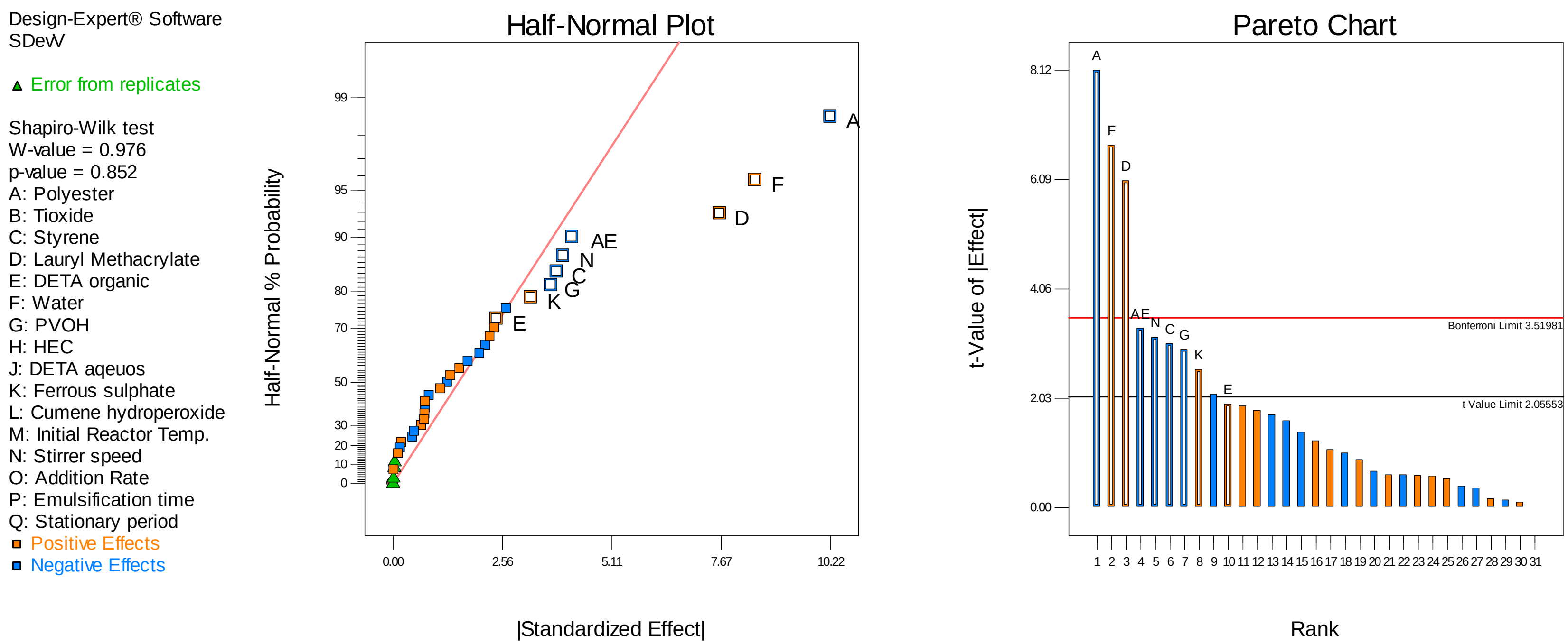
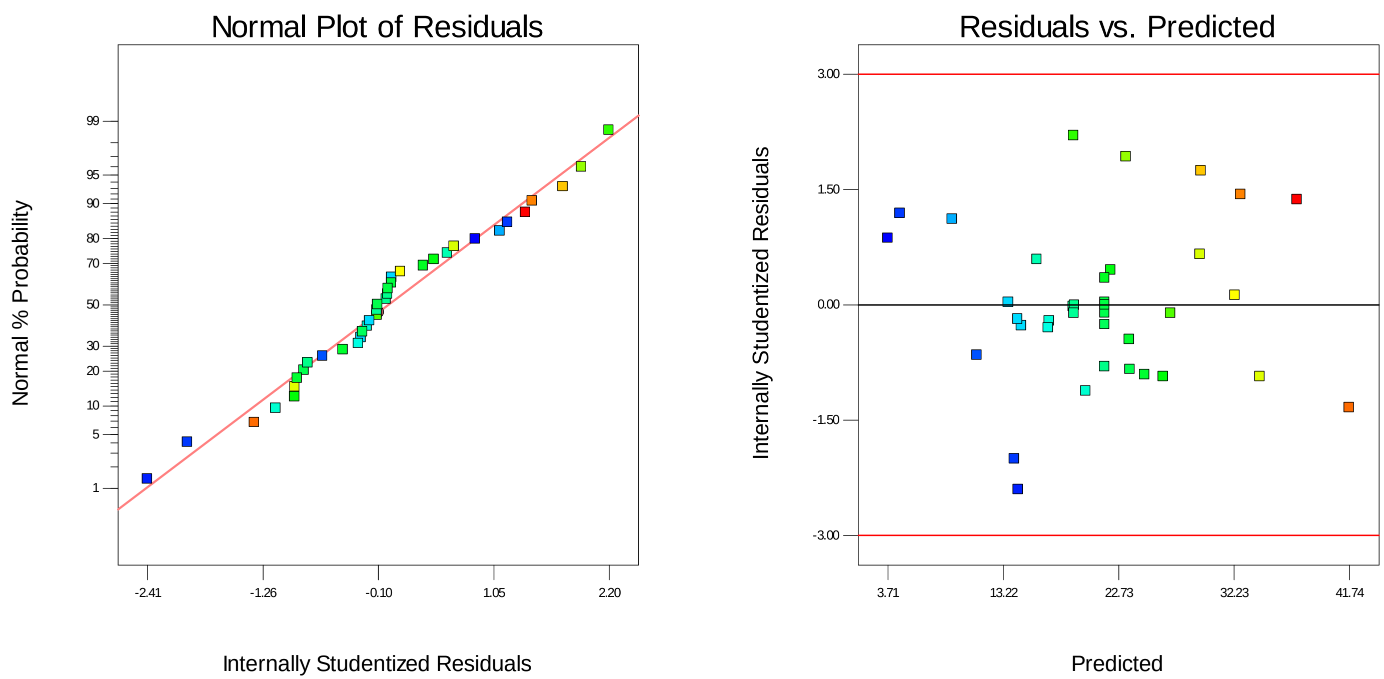
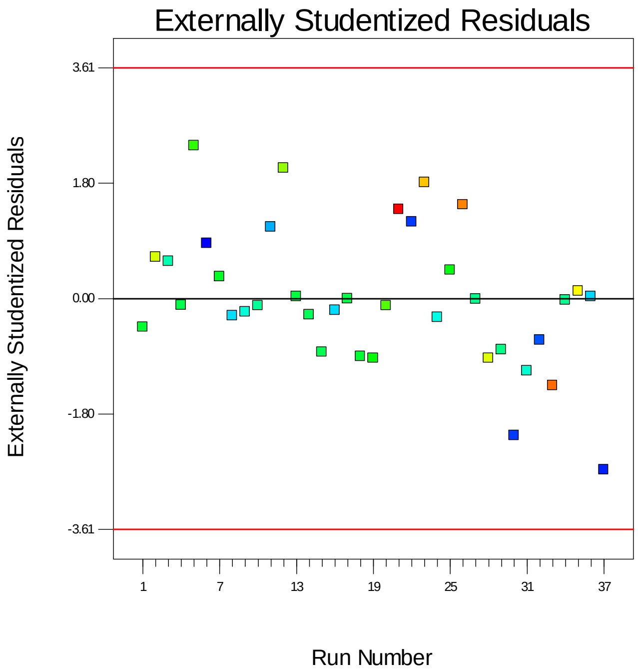
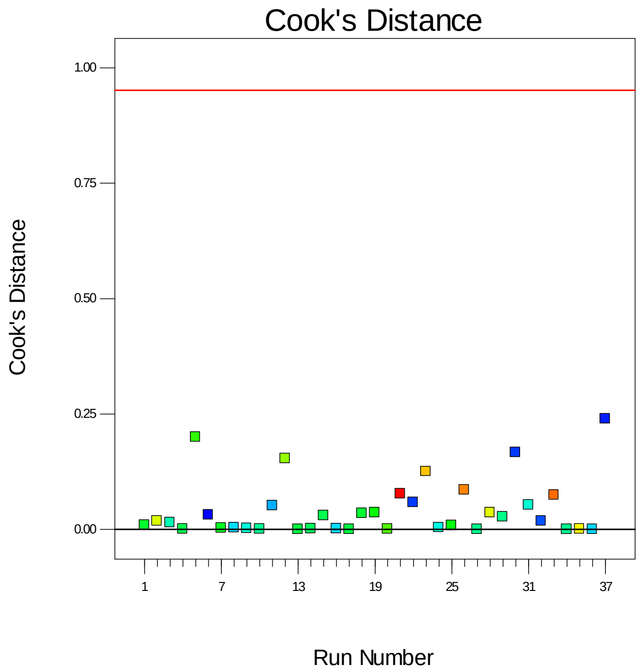


Figure C.4.2: Diagnostic Charts for the SDevV (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.





Externally Studentized Residuals
Externally Studentized Residuals
3.61
1.80
0.00
-1.80
-3.61
1
7
13
19
25
31
37
Run Number



Cook's Distance
Cook's Distance
1.00
0.75
0.50
0.25
0.00
1
7
13
19
25
31
37
Run Number

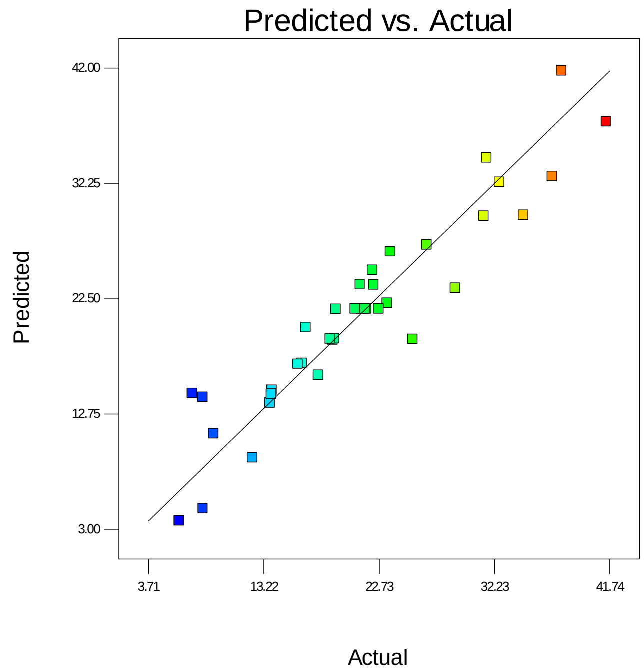
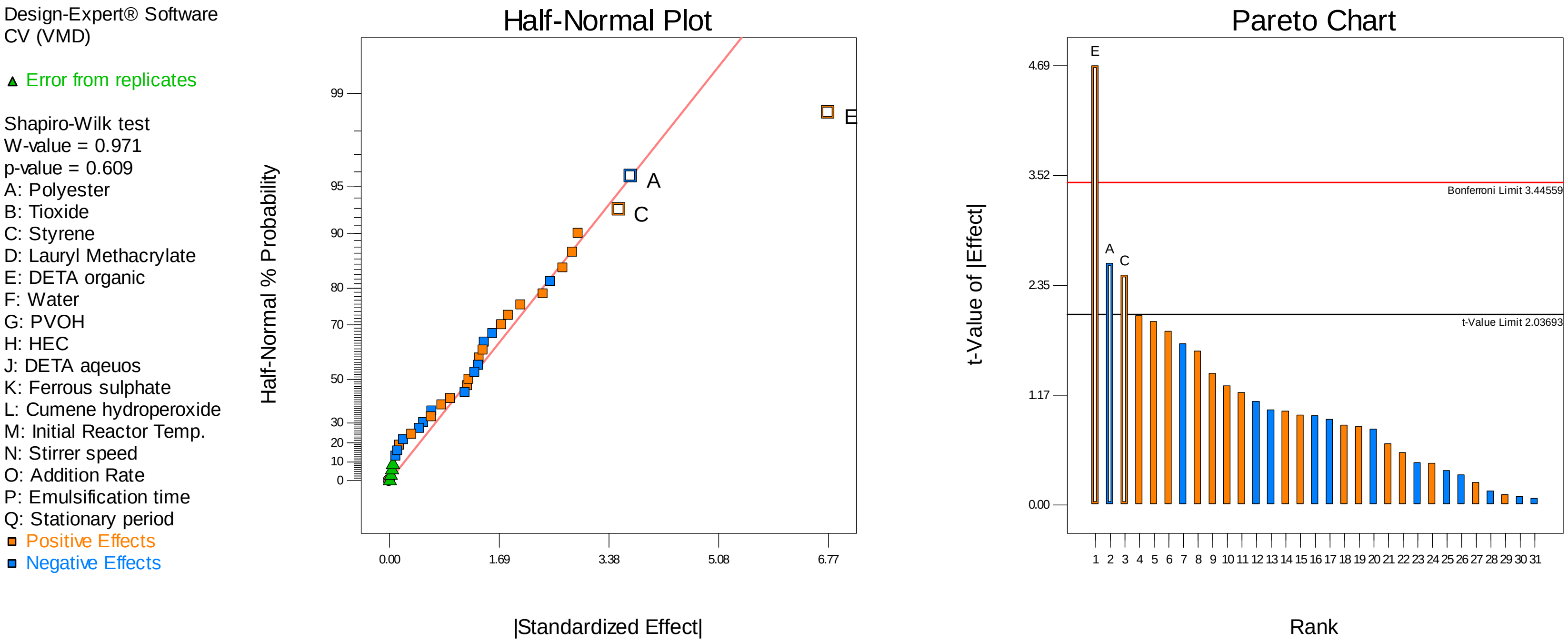
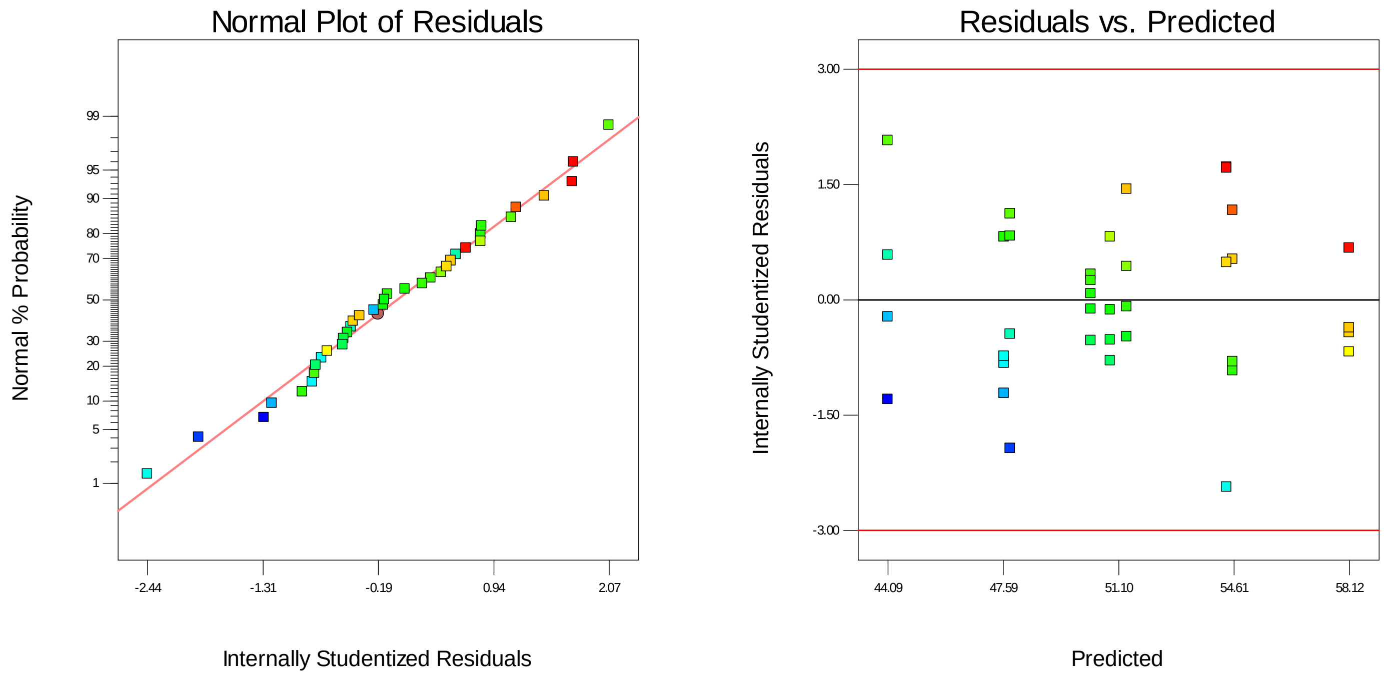
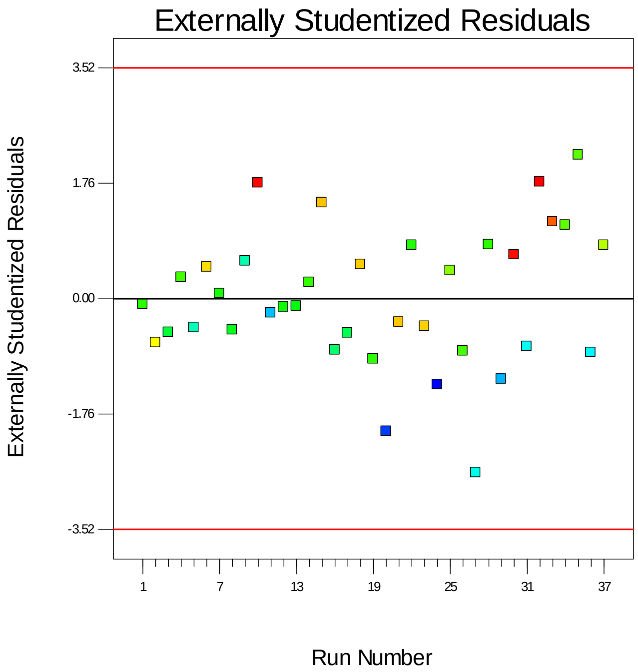

Predicted vs. Actual
42.00
32.25
22.50
12.75
3.00
Predicted
3.71
13.22
22.73
32.23
41.74
Actual

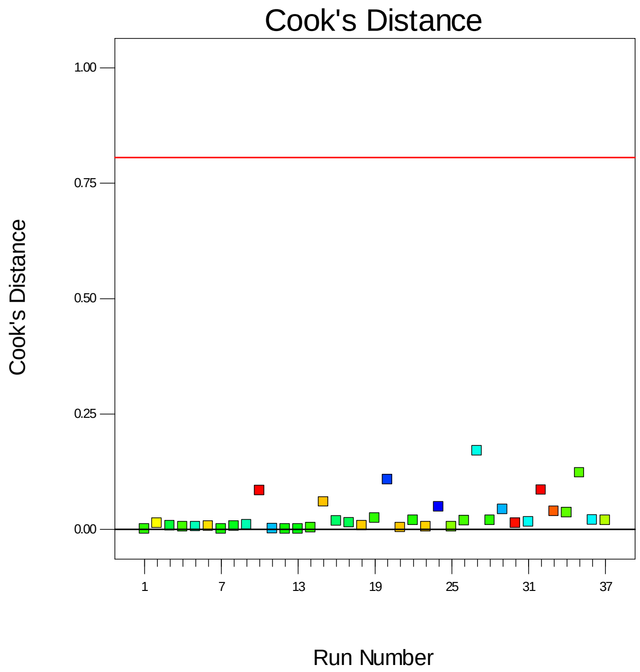
Figure C.5.1: Effect Charts for the %CV (VMD) (a) Half-Normal Plot (b) Pareto Chart

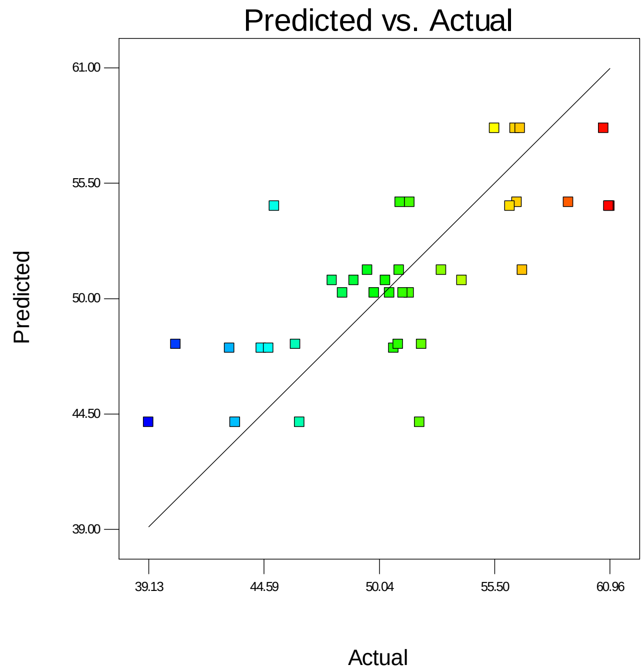


<u>Figure C.5.2:</u> Diagnostic Charts for the %CV (VMD) (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.




Externally Studentized Residuals
Externally Studentized Residuals
3.52
1.76
0.00
-1.76
-3.52
1
7
13
19
25
31
37
Run Number


Cook's Distance
Cook's Distance
1.00
0.75
0.50
0.25
0.00
1
7
13
19
25
31
37
Run Number


Predicted vs. Actual
61.00
55.50
50.00
44.50
39.00
Predicted
39.13
44.59
50.04
55.50
60.96
Actual

<u>Figure C.6.1:</u> Effect Charts for the Brookfield Viscosity (a) Half-Normal Plot (b) Pareto Chart

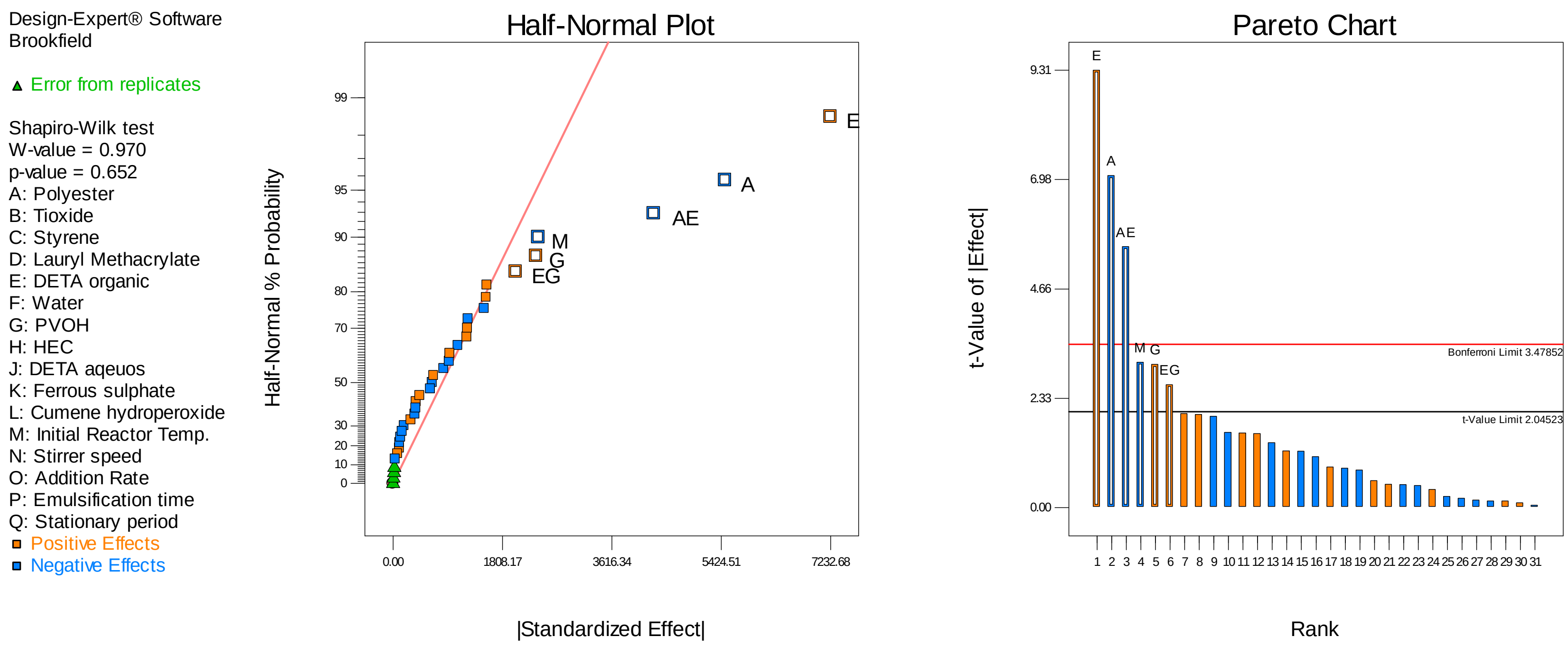
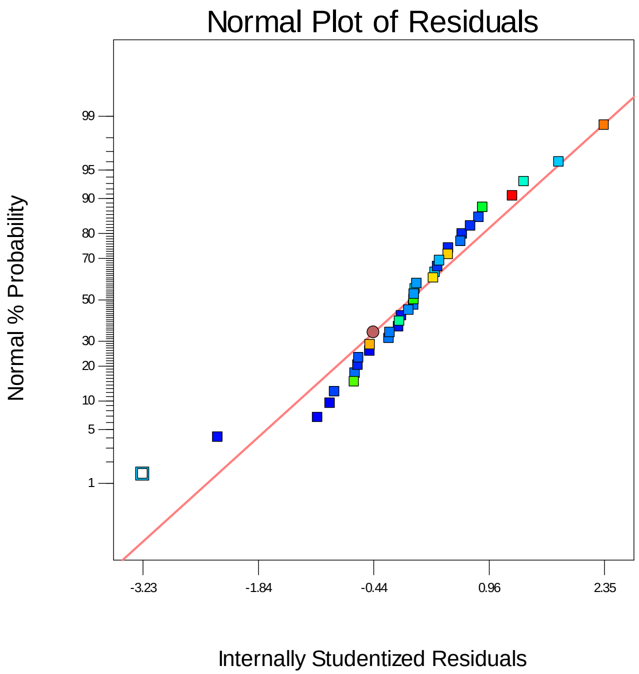
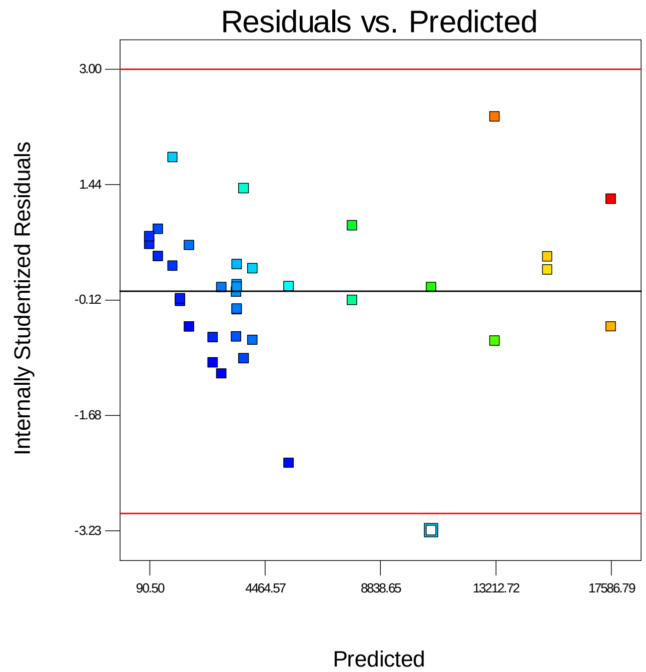
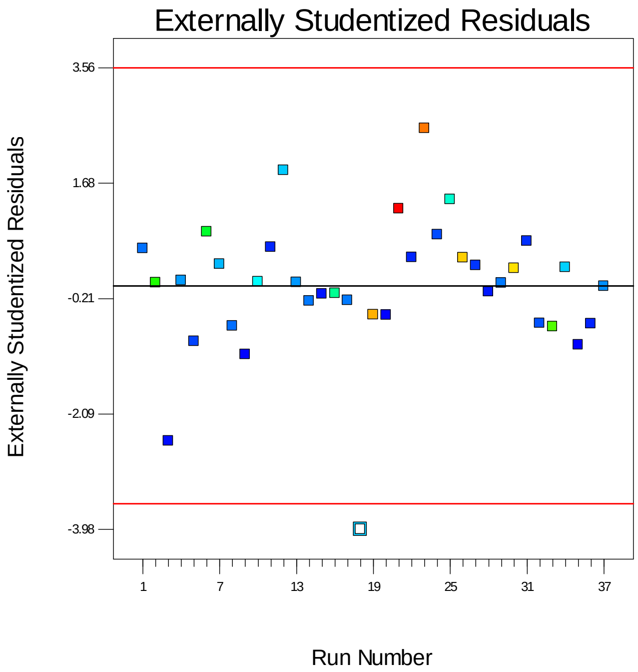
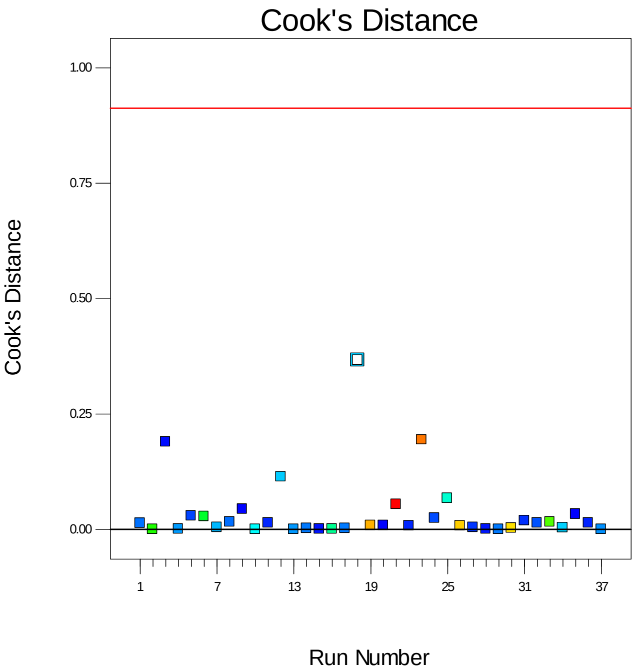


Figure C.6.2: Diagnostic Charts for the Brookfield Viscosity (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
3.56
1.68
-0.21
-2.09
-3.98
Externally Studentized Residuals
1
7
13
19
25
31
37
Run Number


Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
7
13
19
25
31
37
Run Number

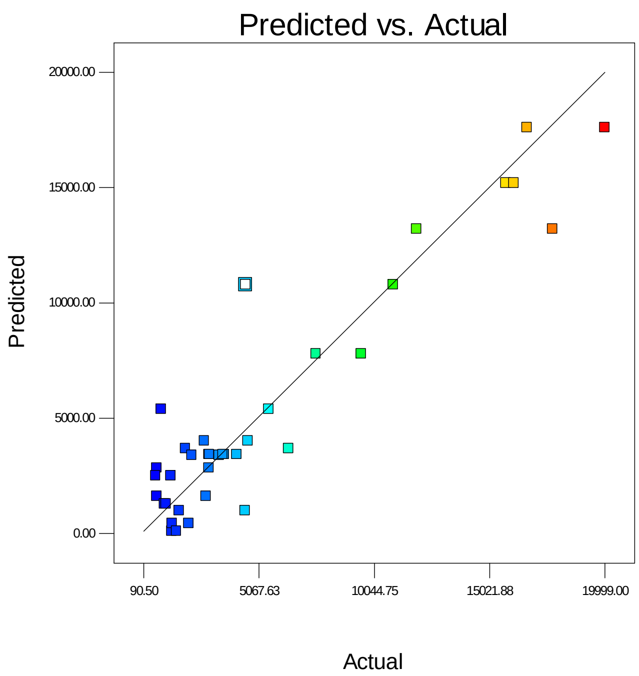

Predicted vs. Actual
20000.00
15000.00
10000.00
5000.00
0.00
Predicted
90.50
5067.63
10044.75
15021.88
19999.00
Actual

Figure C.7.1: Effect Charts for the SG (a) Half-Normal Plot (b) Pareto Chart

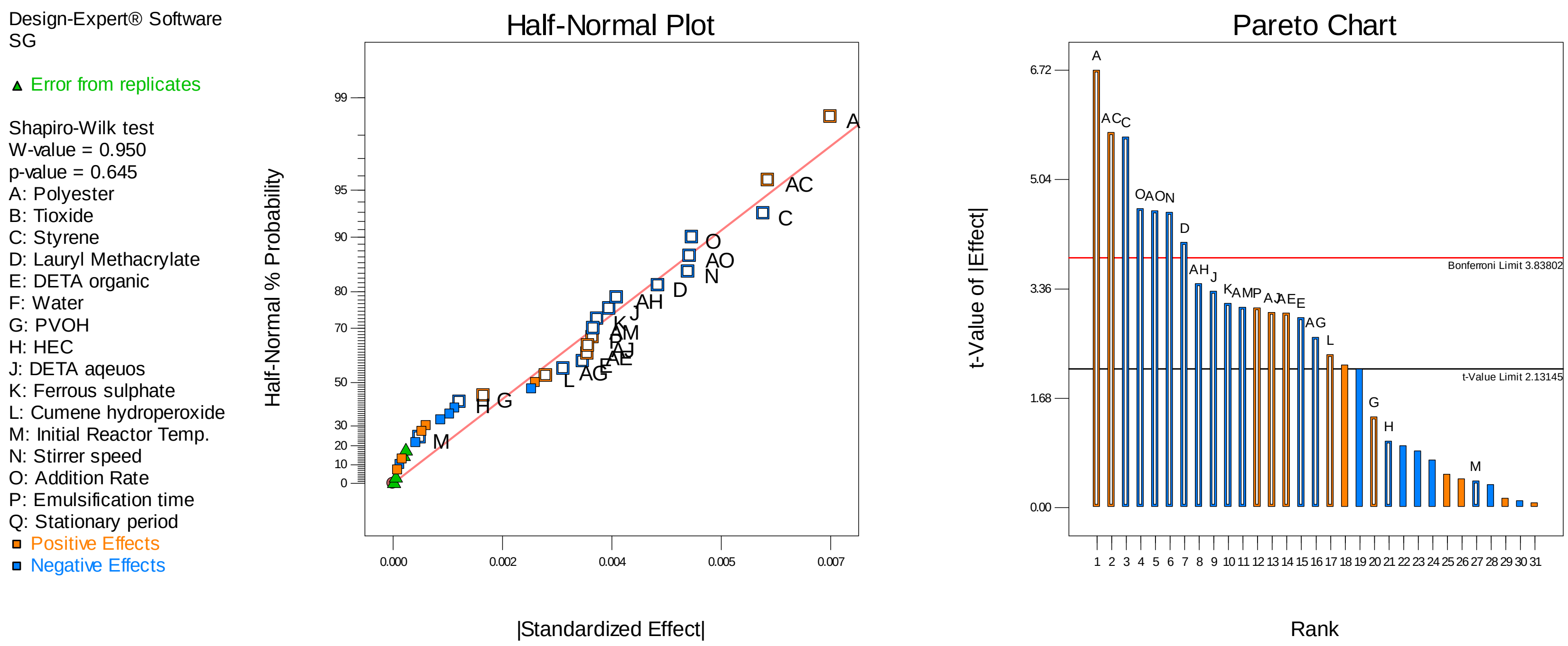
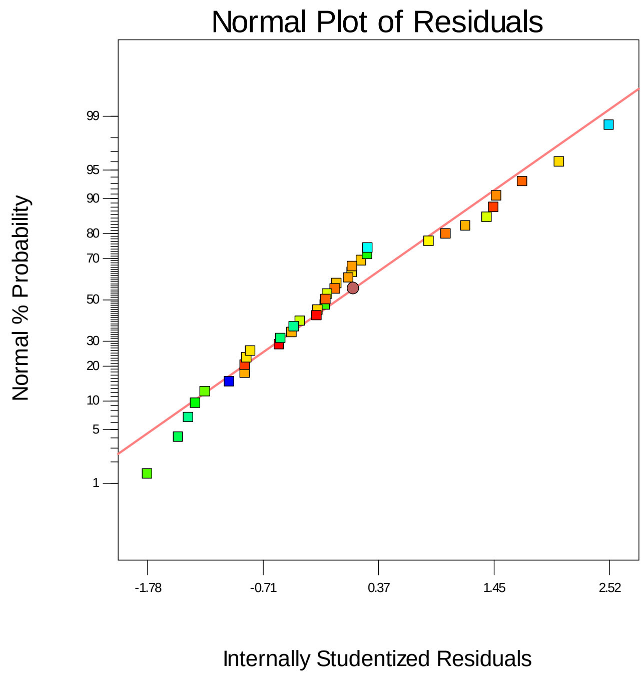
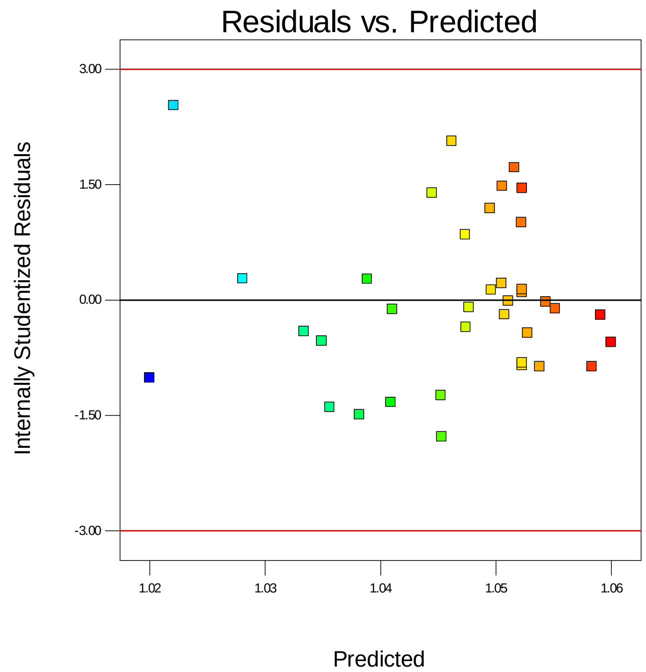
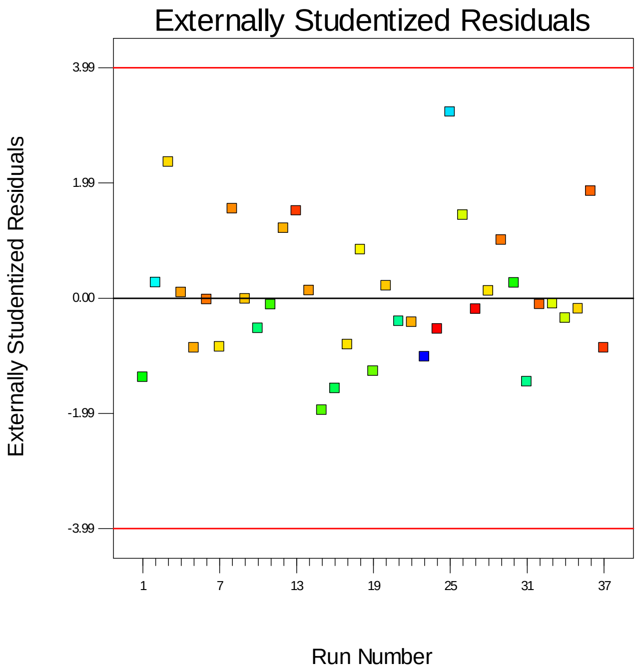
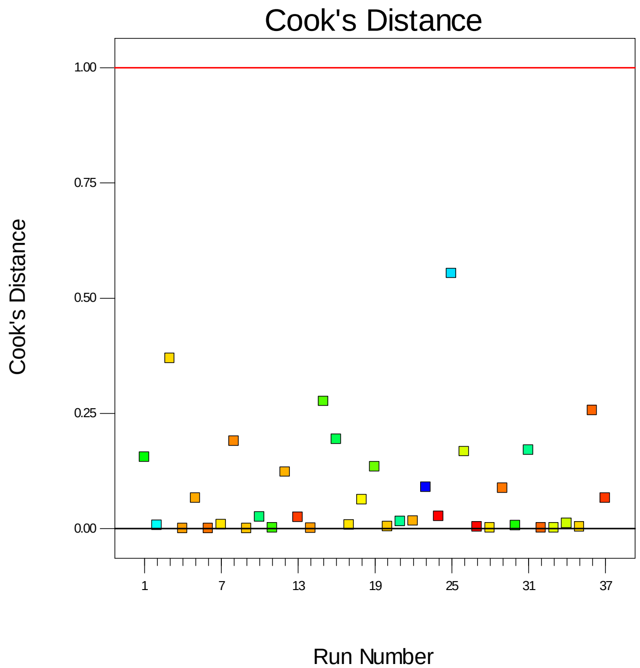


Figure C.7.2: Diagnostic Charts for the SG (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
3.99
1.99
0.00
-1.99
-3.99
Externally Studentized Residuals
1
7
13
19
25
31
37
Run Number


Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
7
13
19
25
31
37
Run Number

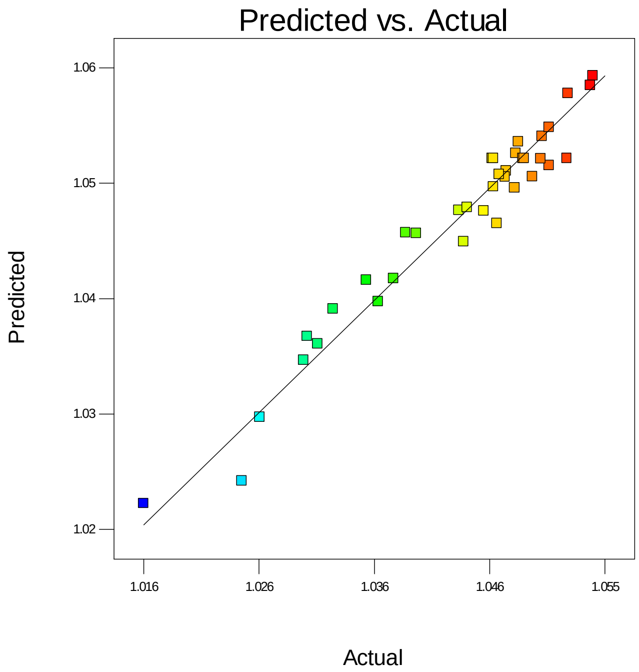

Predicted vs. Actual
Predicted
Actual
1.06
1.05
1.04
1.03
1.02
1.016
1.026
1.036
1.046
1.055

Figure C.8.1: Effect Charts for the %NVC (a) Half-Normal Plot (b) Pareto Chart

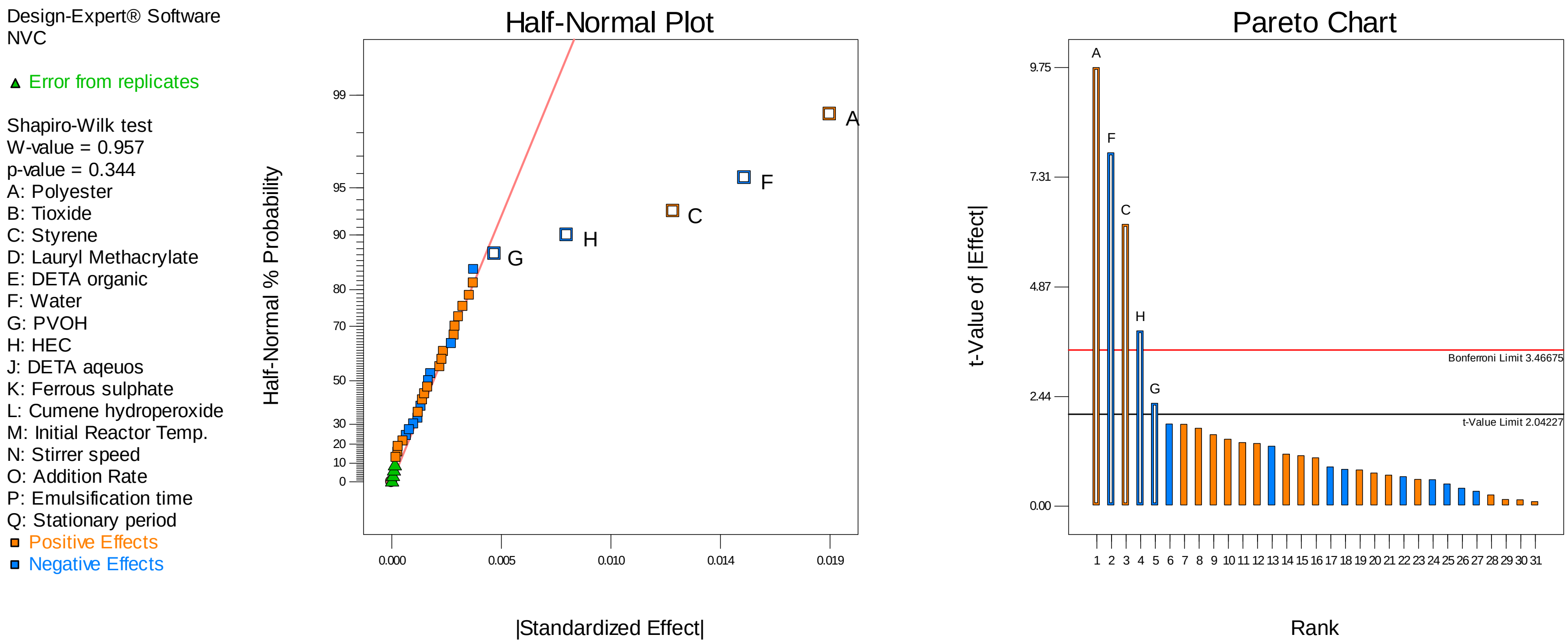
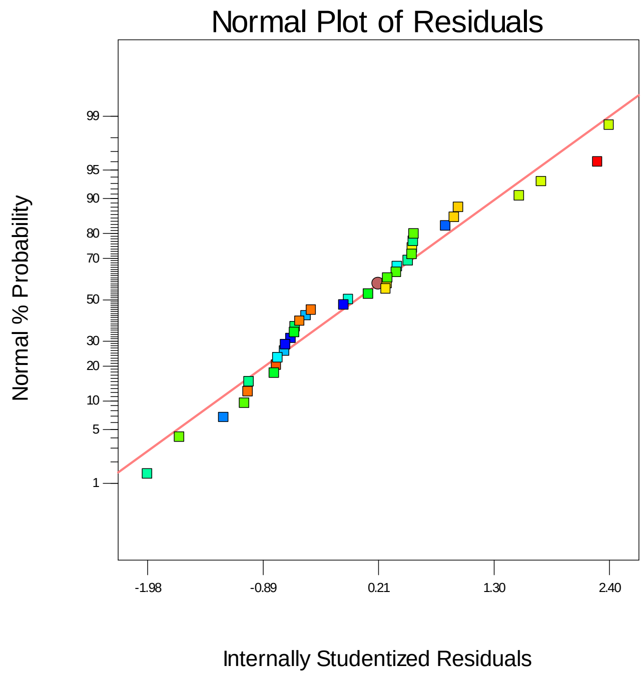
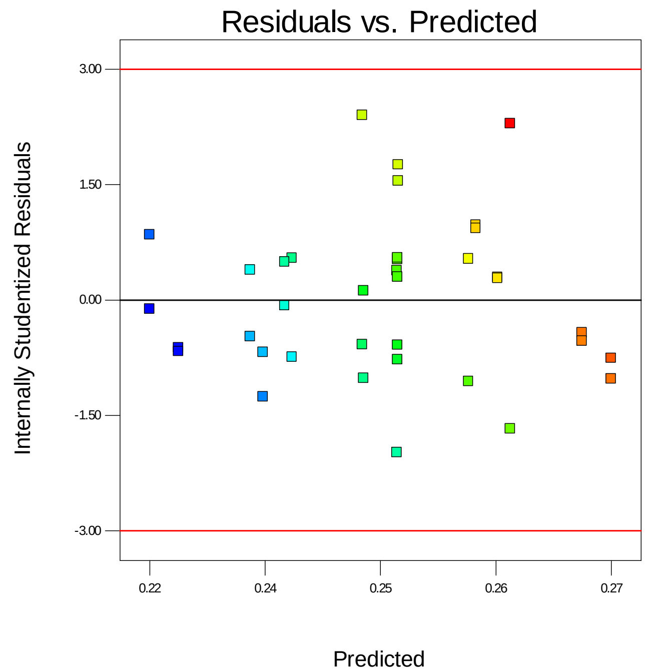
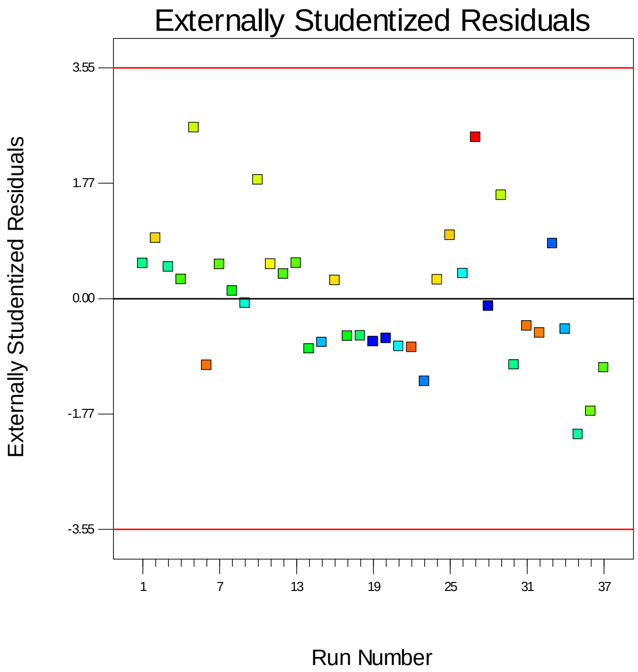


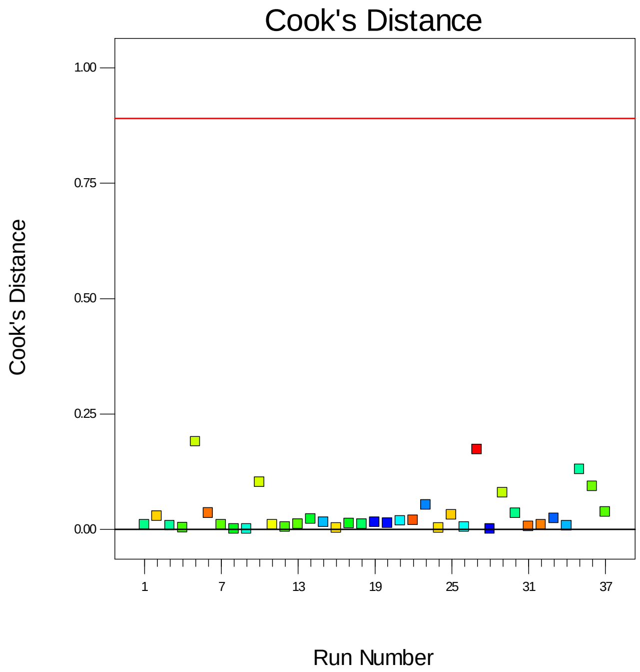
Figure C.8.2: Diagnostic Charts for the %NVC (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.



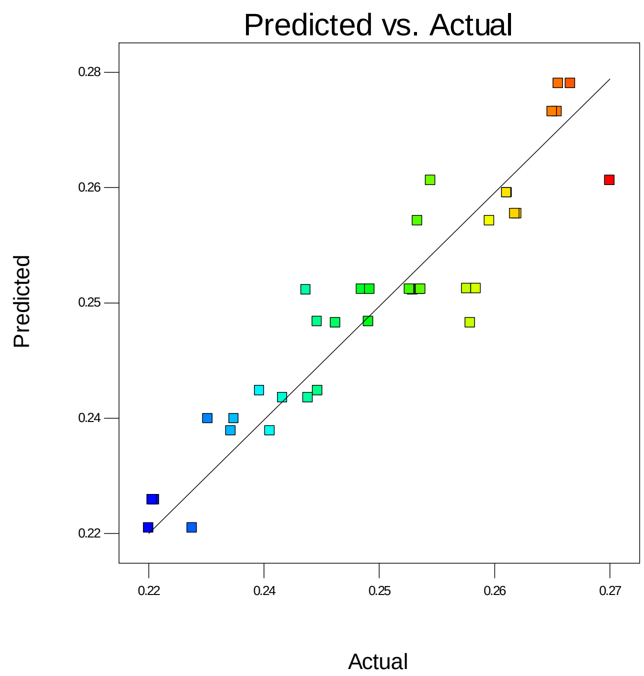




Externally Studentized Residuals
3.55
1.77
0.00
-1.77
-3.55
Externally Studentized Residuals
1
7
13
19
25
31
37
Run Number



Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
7
13
19
25
31
37
Run Number



Predicted vs. Actual
0.28
0.26
0.25
0.24
0.22
Predicted
0.22
0.24
0.25
0.26
0.27
Actual

Figure C.9.1: Effect Charts for the SMD (a) Half-Normal Plot (b) Pareto Chart

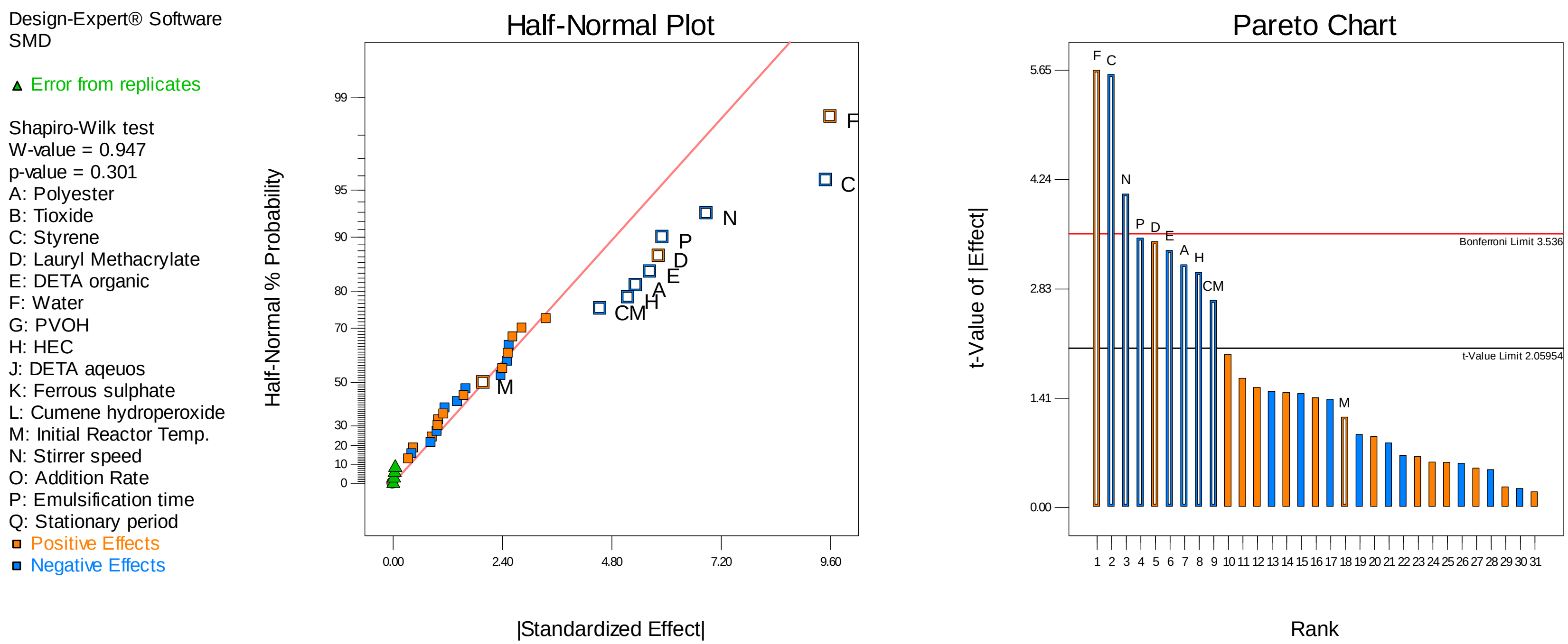
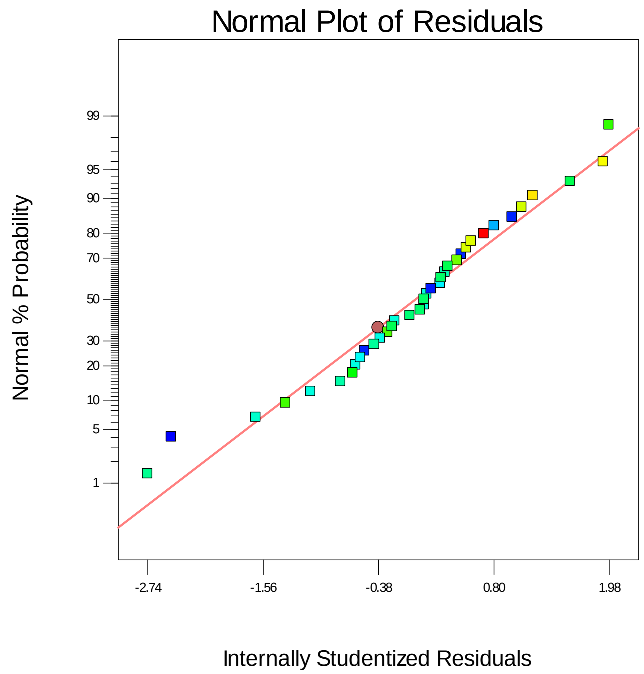
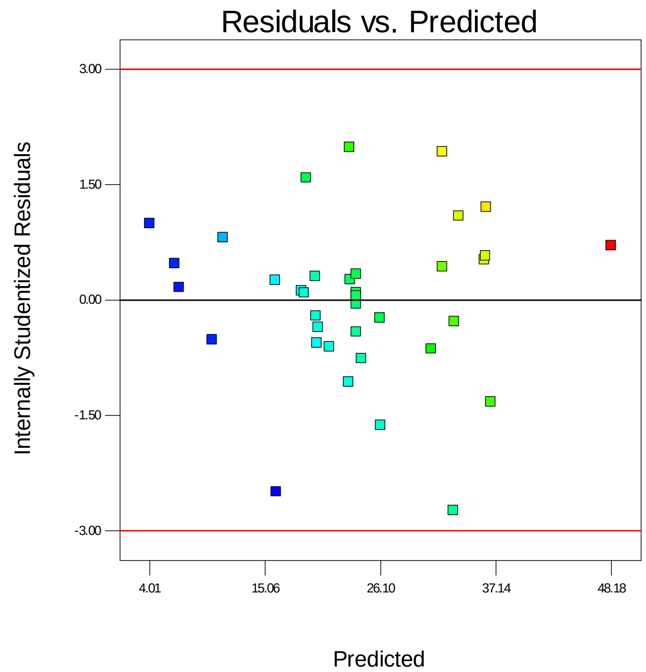
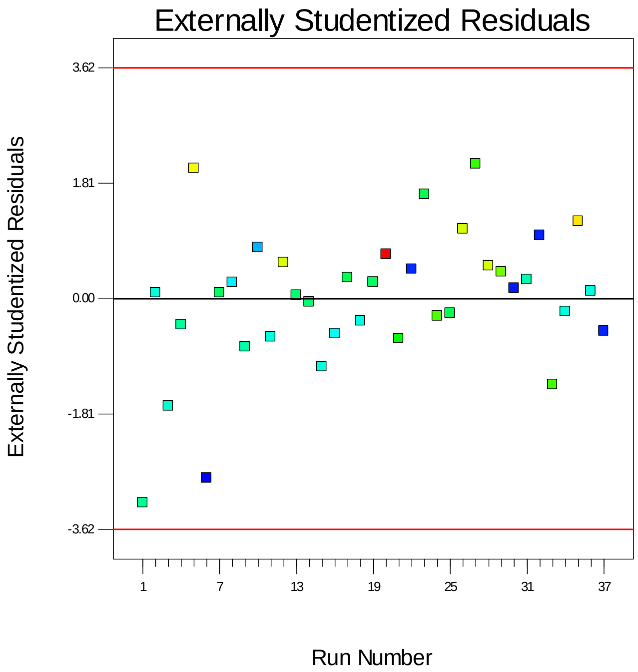
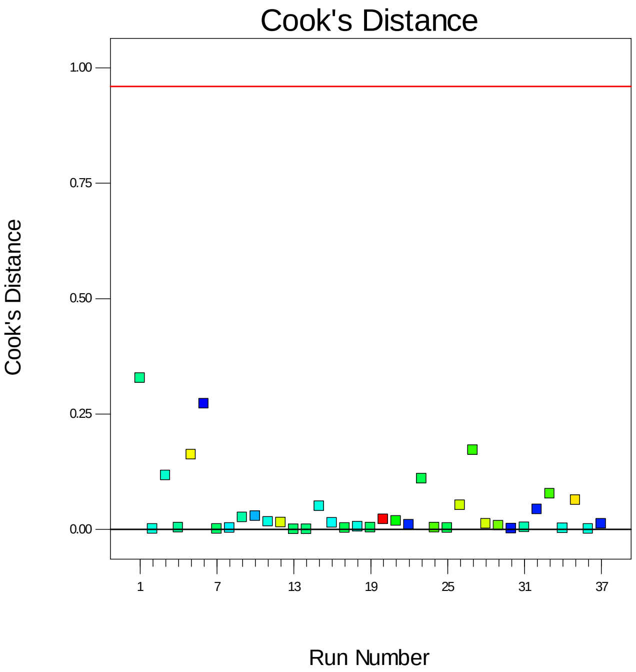


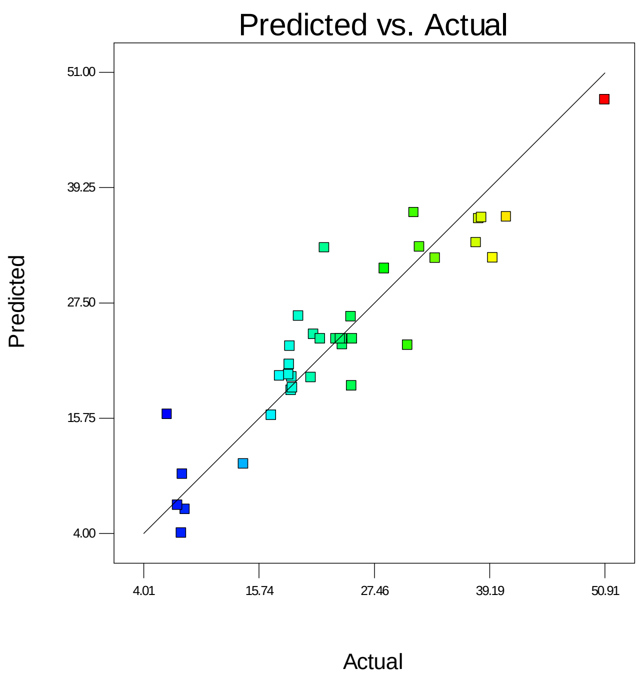
Figure C.9.2: Diagnostic Charts for the SMD (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
Externally Studentized Residuals
3.62
1.81
0.00
-1.81
-3.62
1
7
13
19
25
31
37
Run Number


Cook's Distance
Cook's Distance
1.00
0.75
0.50
0.25
0.00
1
7
13
19
25
31
37
Run Number



Predicted vs. Actual
51.00
39.25
27.50
15.75
4.00
Predicted
4.01
15.74
27.46
39.19
50.91
Actual

Figure C.10.1: Effect Charts for the SDevS (a) Half-Normal Plot (b) Pareto Chart

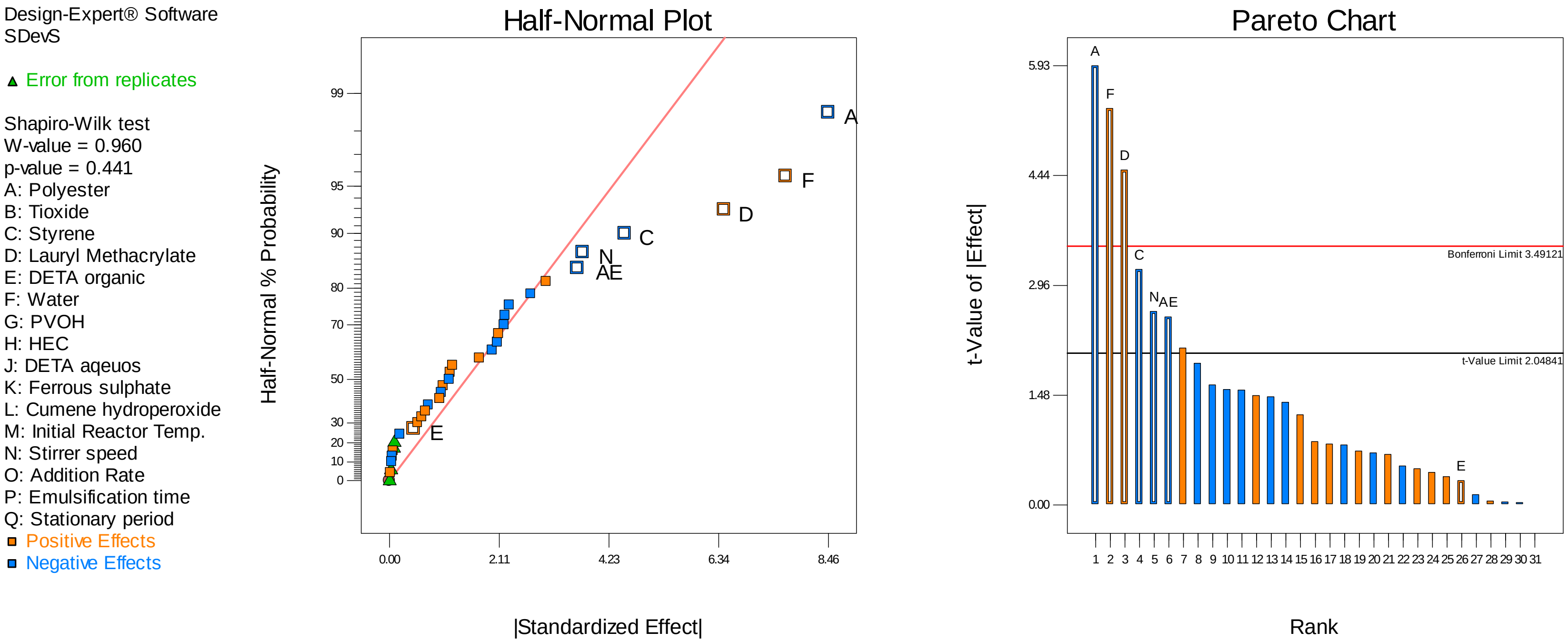
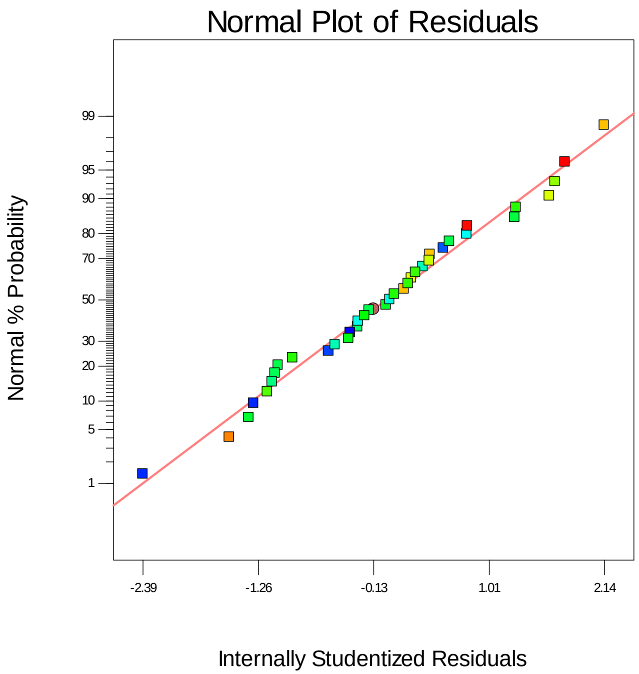
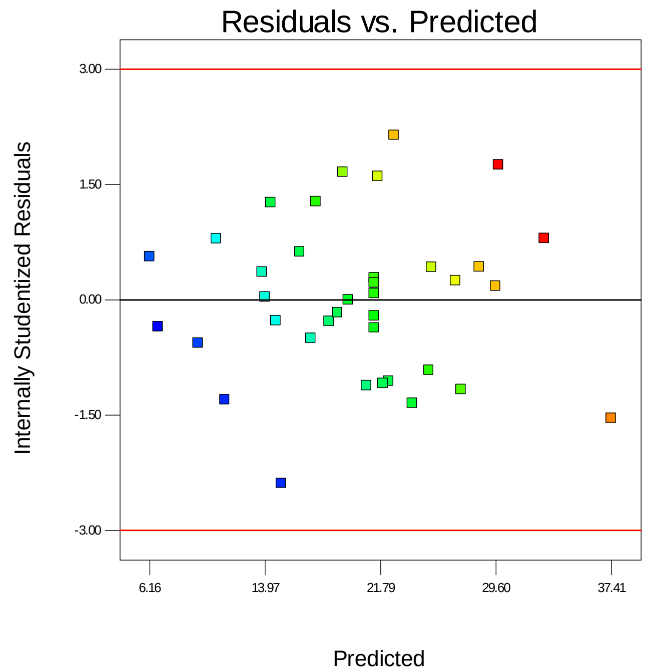
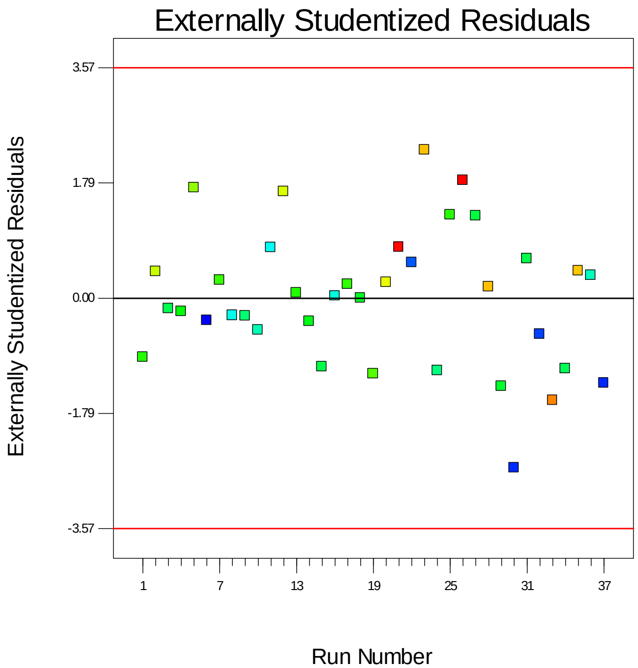


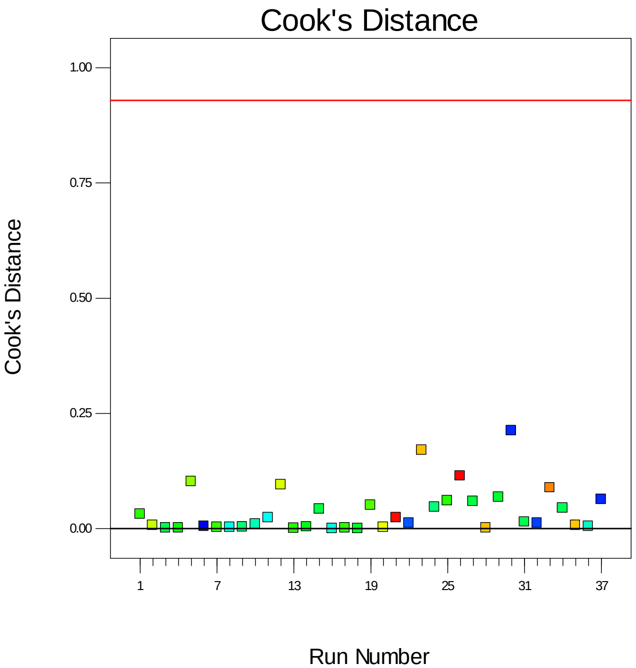
Figure C.10.2: Diagnostic Charts for the SDevS (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.



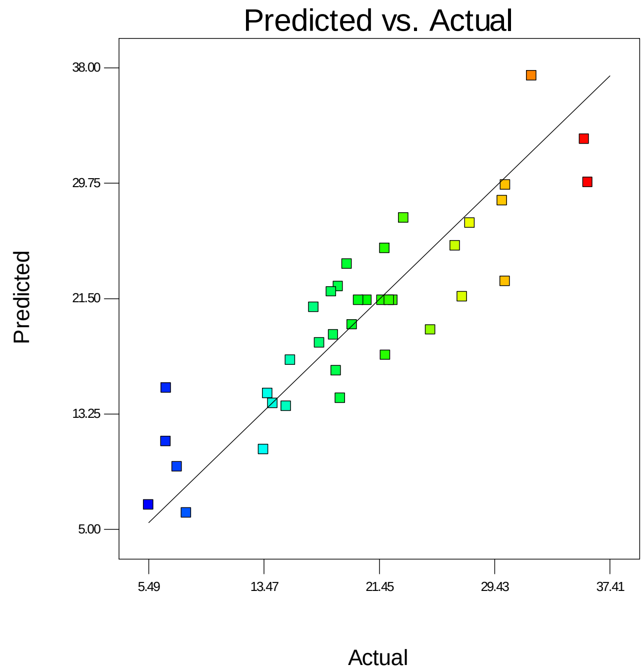




Externally Studentized Residuals
3.57
1.79
0.00
-1.79
-3.57
Externally Studentized Residuals
1
7
13
19
25
31
37
Run Number



Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
7
13
19
25
31
37
Run Number


Predicted vs. Actual
Predicted
Actual
38.00
29.75
21.50
13.25
5.00
5.49
13.47
21.45
29.43
37.41

<u>Figure C.11.1</u>: Effect Charts for the %CV (SMD) (a) Half-Normal Plot (b) Pareto Chart

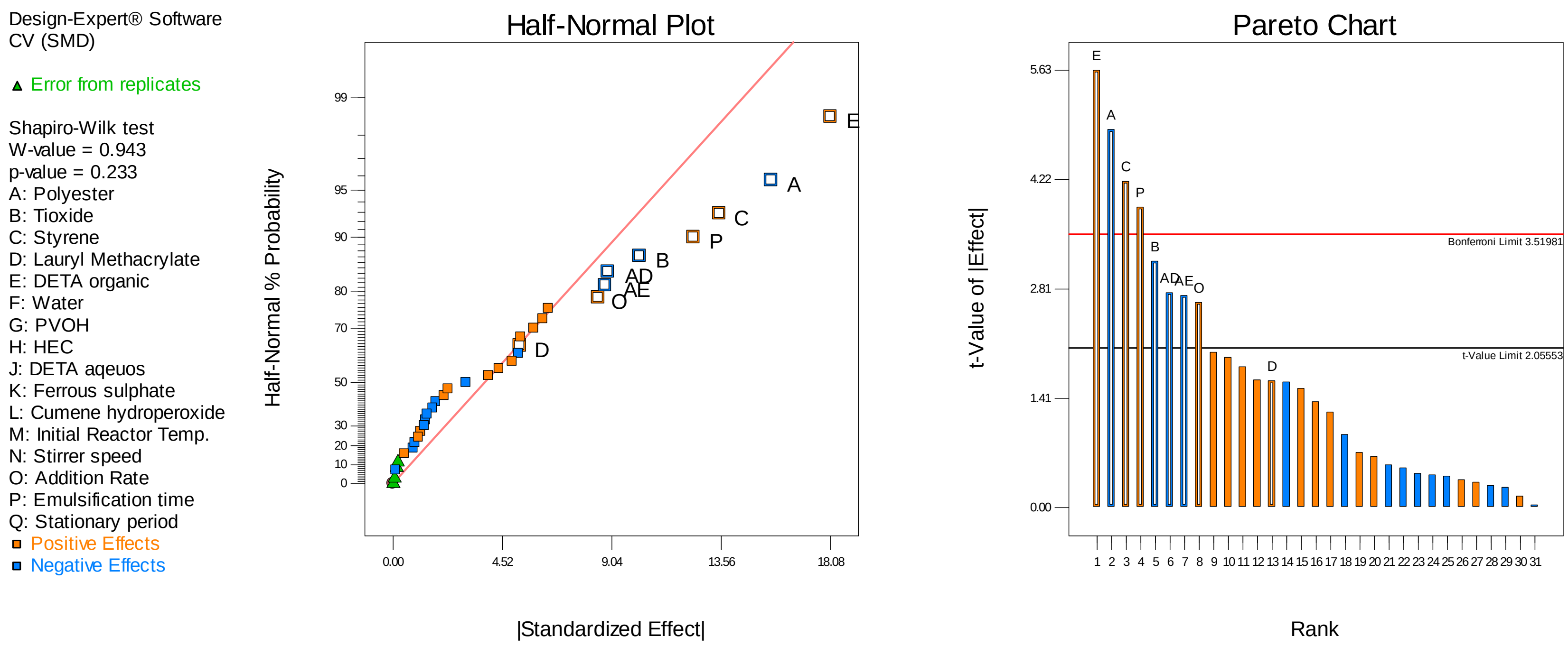
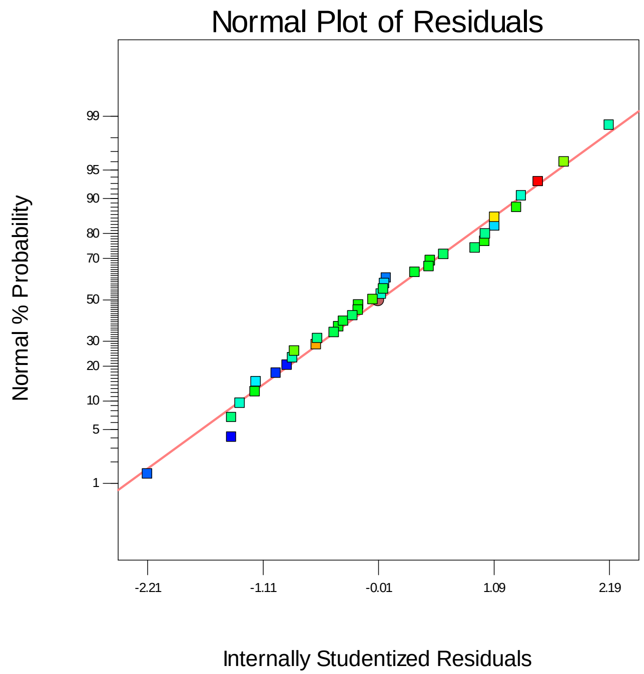
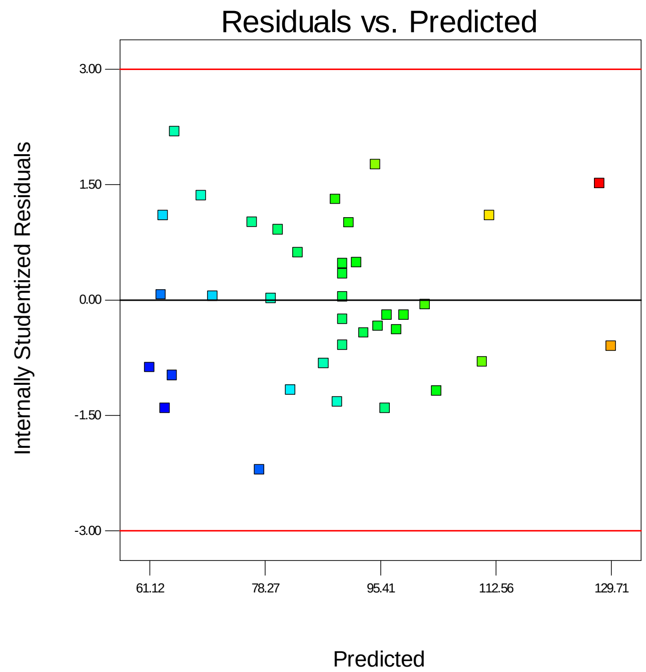
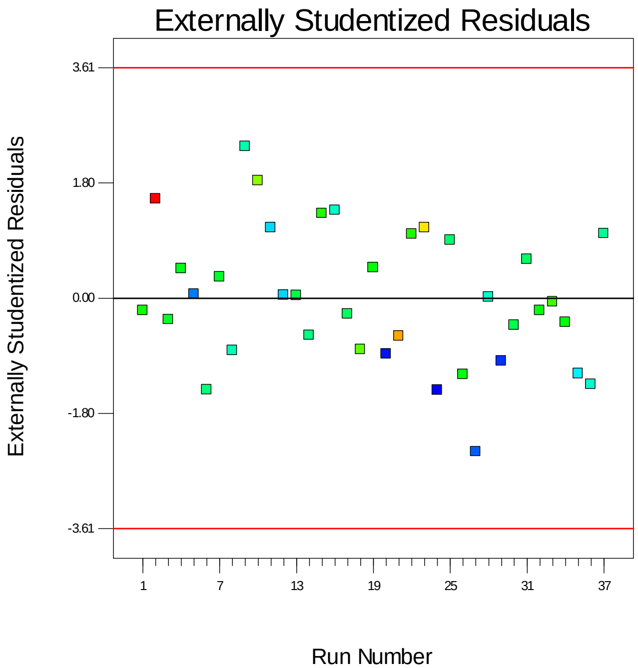
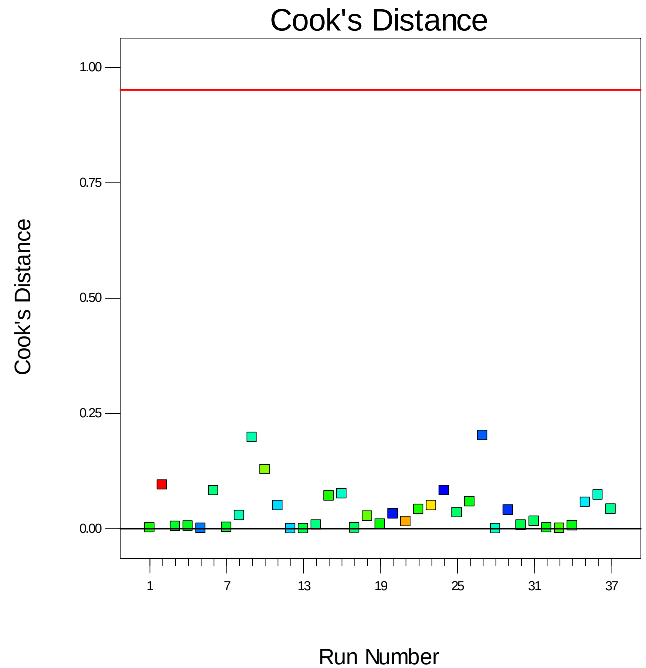


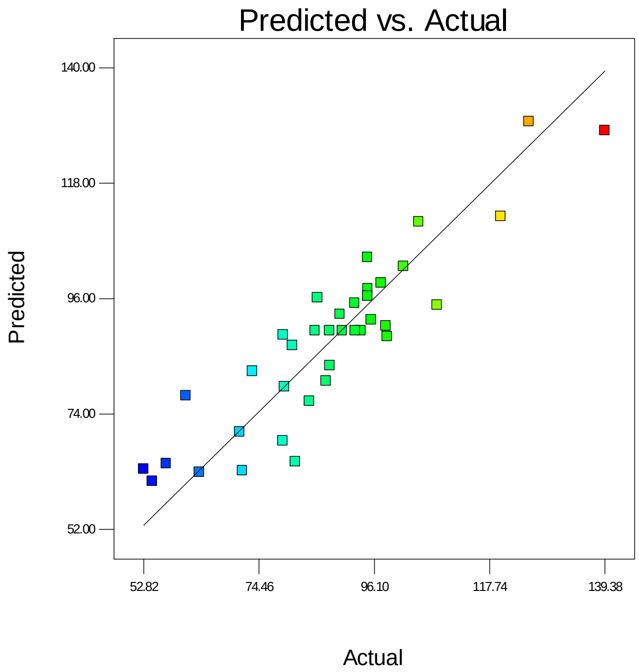
Figure C.11.2: Diagnostic Charts for the %CV (SMD) (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
Externally Studentized Residuals
3.61
1.80
0.00
-1.80
-3.61
1
7
13
19
25
31
37
Run Number


Cook's Distance
Cook's Distance
1.00
0.75
0.50
0.25
0.00
1
7
13
19
25
31
37
Run Number



Predicted vs. Actual
140.00
118.00
96.00
74.00
52.00
Predicted
52.82
74.46
96.10
117.74
139.38
Actual

Figure C.12.1: Effect Charts for the CR (a) Half-Normal Plot (b) Pareto Chart

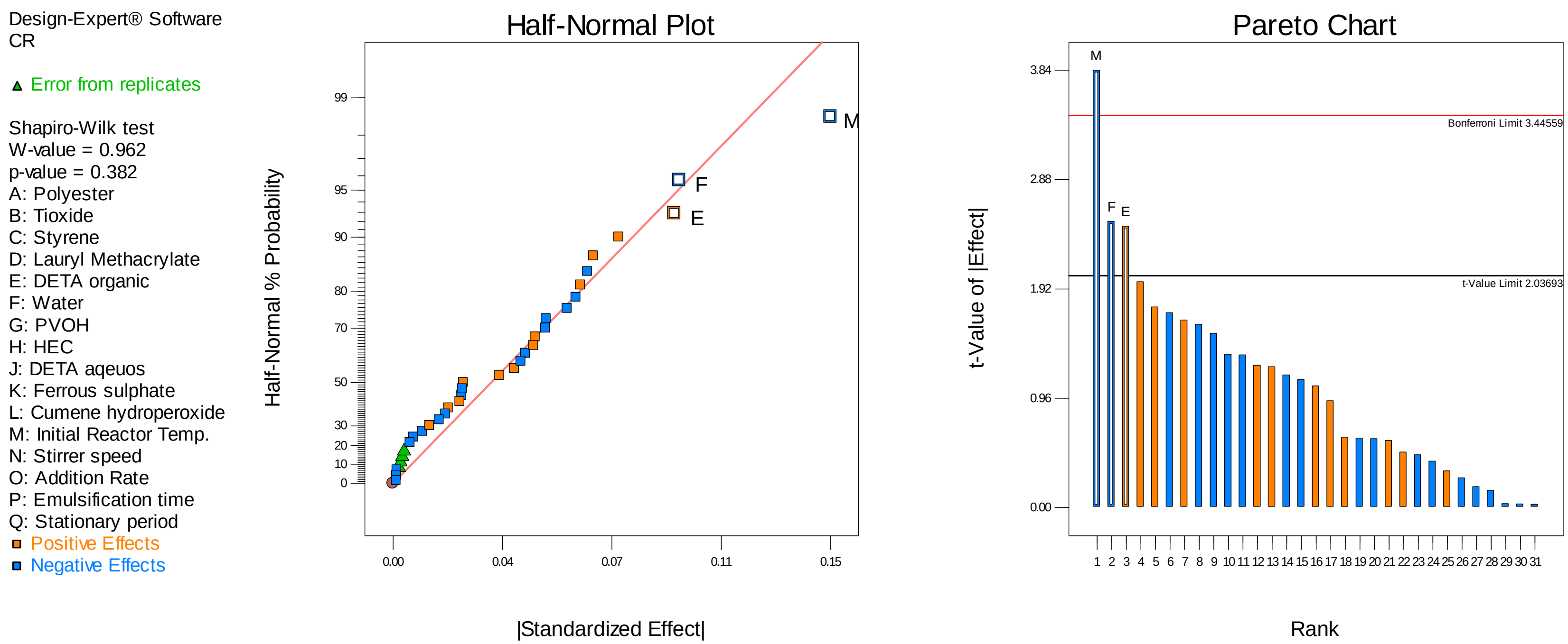
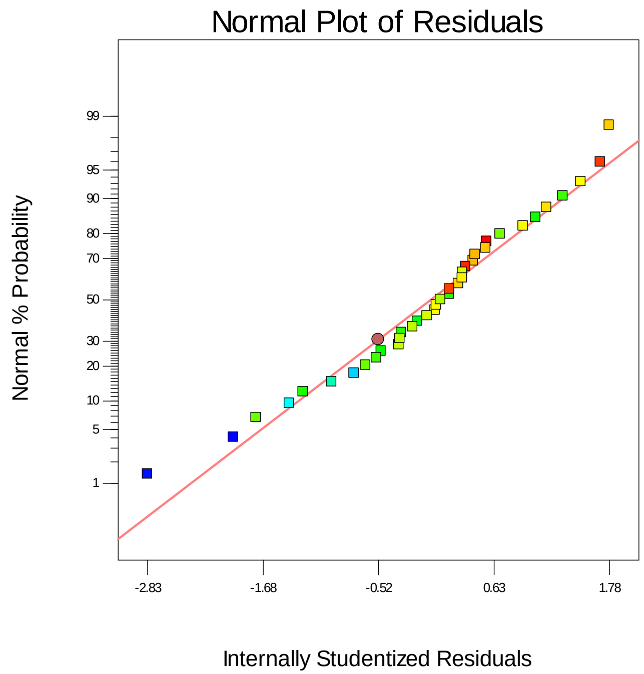
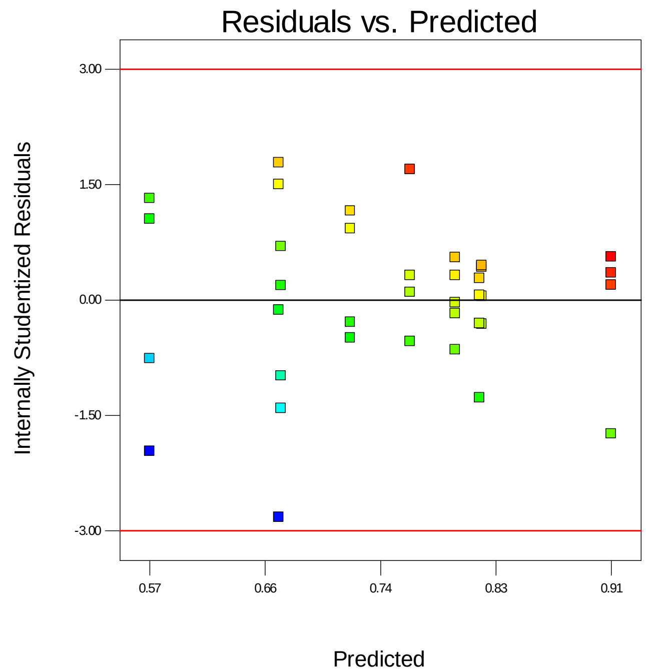
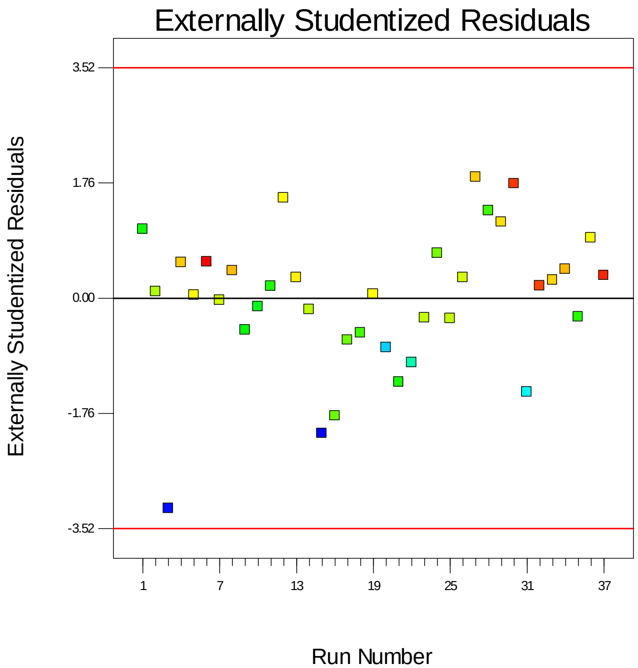
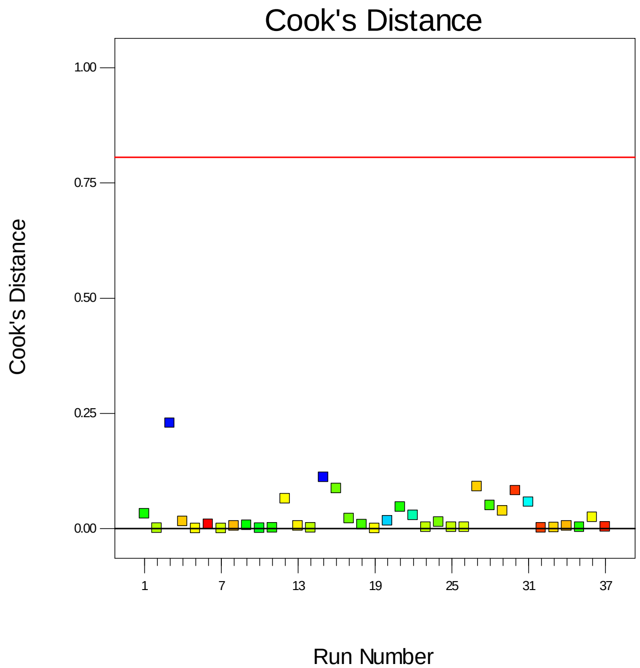


Figure C.12.2: Diagnostic Charts for the CR (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
Externally Studentized Residuals
3.52
1.76
0.00
-1.76
-3.52
1
7
13
19
25
31
37
Run Number


Cook's Distance
Cook's Distance
1.00
0.75
0.50
0.25
0.00
1
7
13
19
25
31
37
Run Number

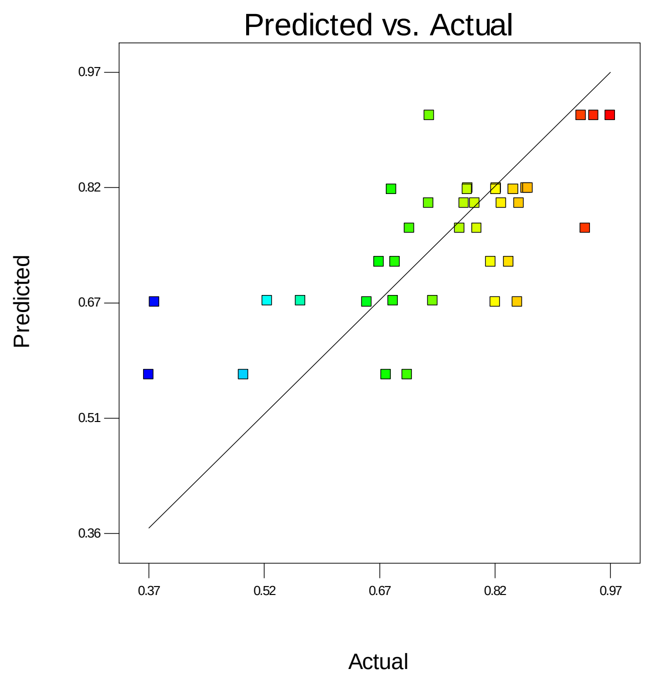

Predicted vs. Actual
0.97
0.82
0.67
0.51
0.36
Predicted
0.37
0.52
0.67
0.82
0.97
Actual

Figure C.13.1: Effect Charts for the Coarseness of Paint (a) Half-Normal P lot (b) Pareto Chart

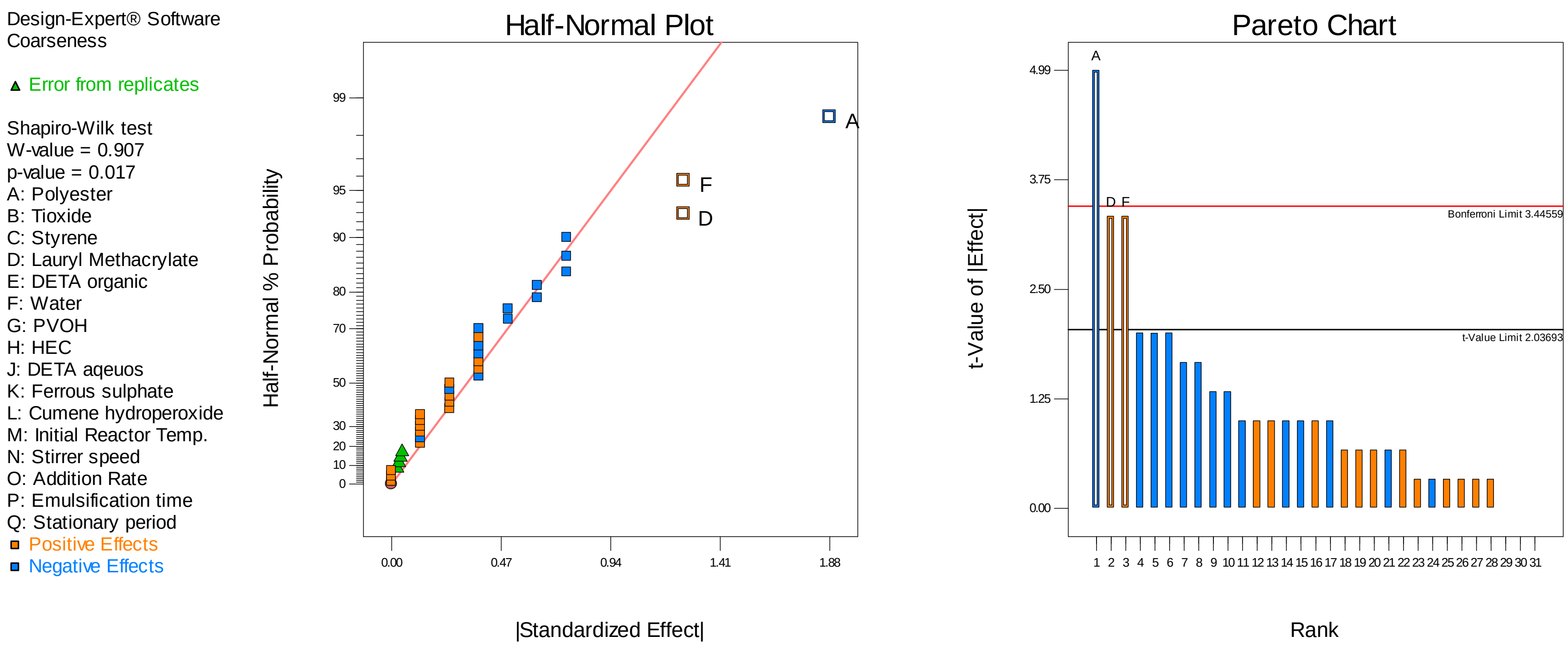
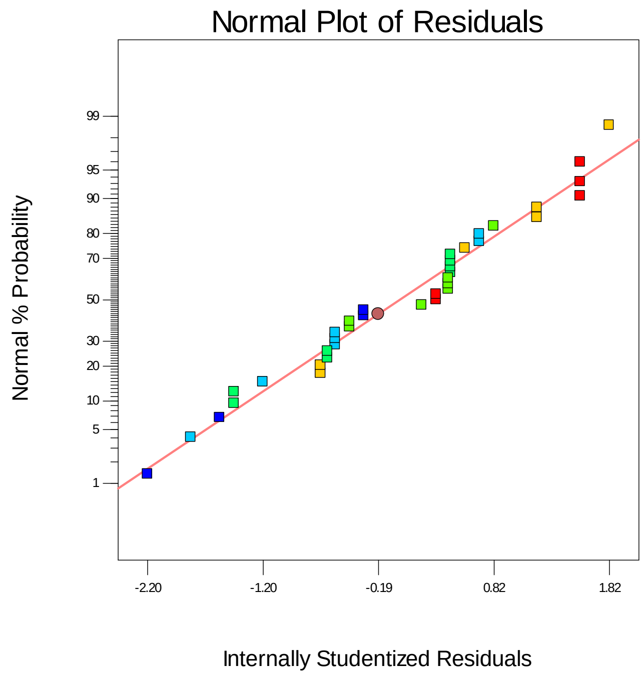
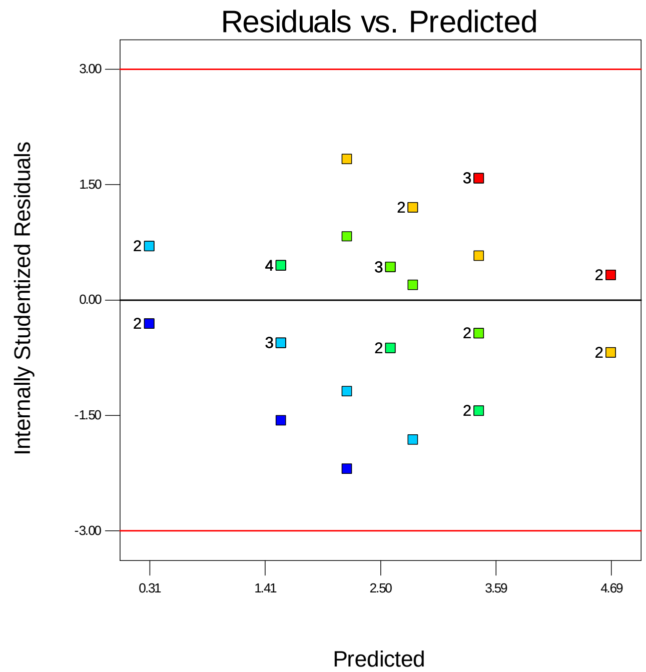
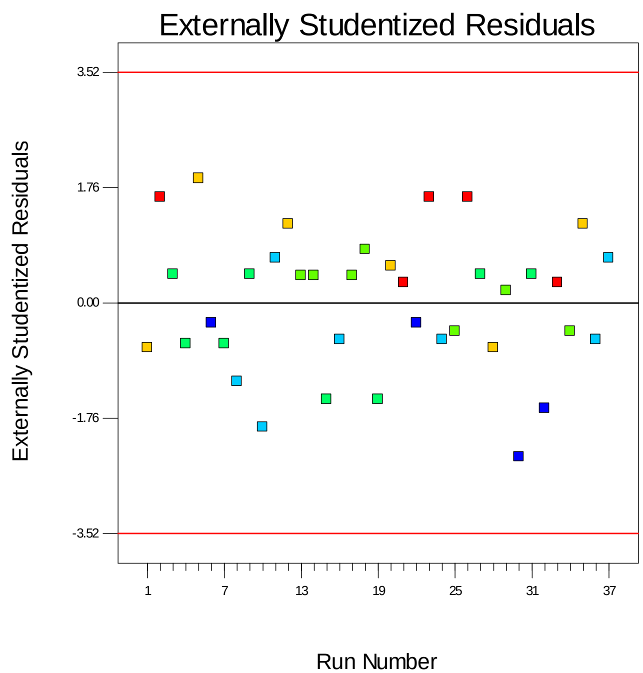
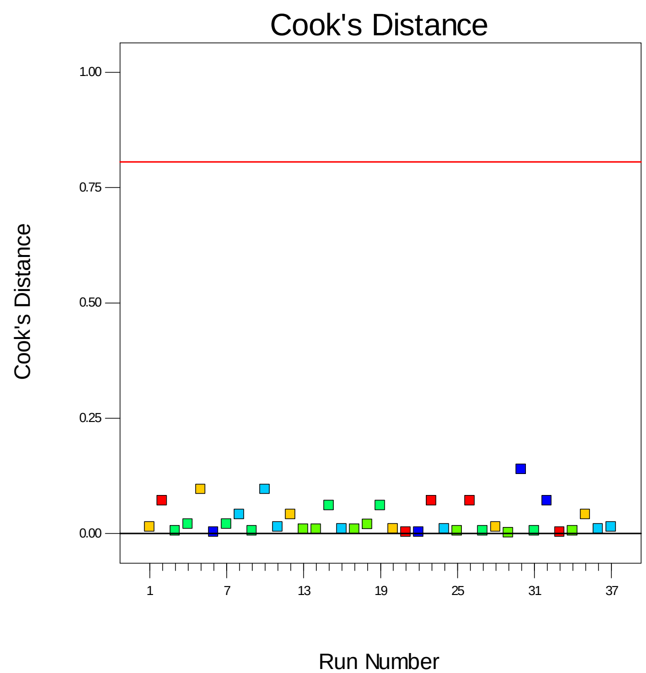


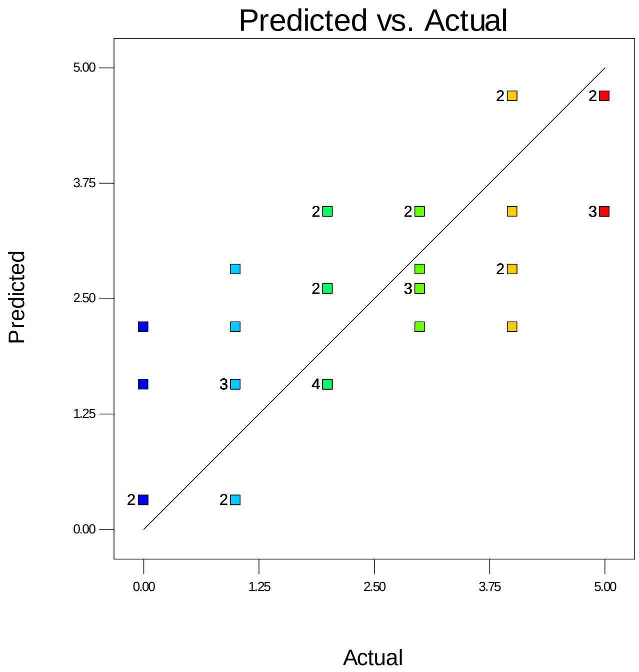
Figure C.13.2: Diagnostic Charts for the Coarseness of Paint (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
Externally Studentized Residuals
3.52
1.76
0.00
-1.76
-3.52
1
7
13
19
25
31
37
Run Number


Cook's Distance
Cook's Distance
1.00
0.75
0.50
0.25
0.00
1
7
13
19
25
31
37
Run Number



Predicted vs. Actual
Predicted
Actual
5.00
3.75
2.50
1.25
0.00
0.00
1.25
2.50
3.75
5.00

Figure C.14.1: Effect Charts for the Tint Strength (a) Half-Normal Plot (b) Pareto Chart

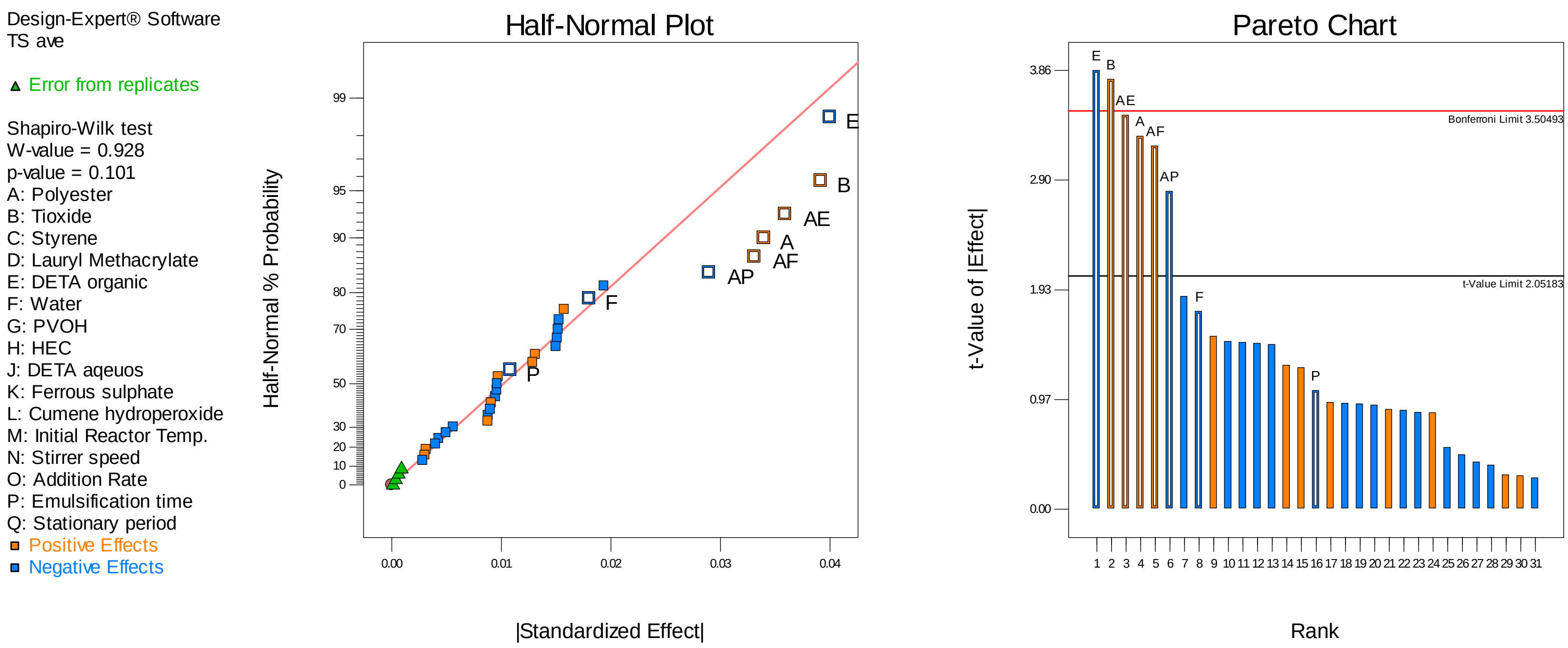
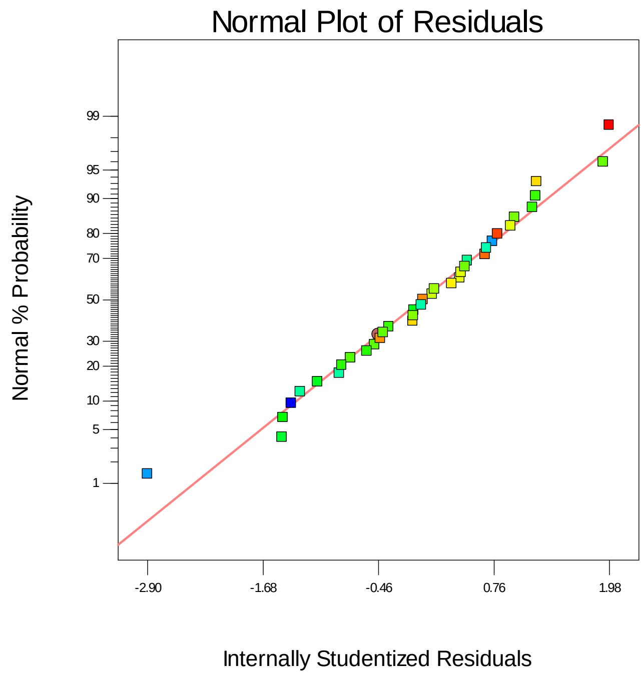
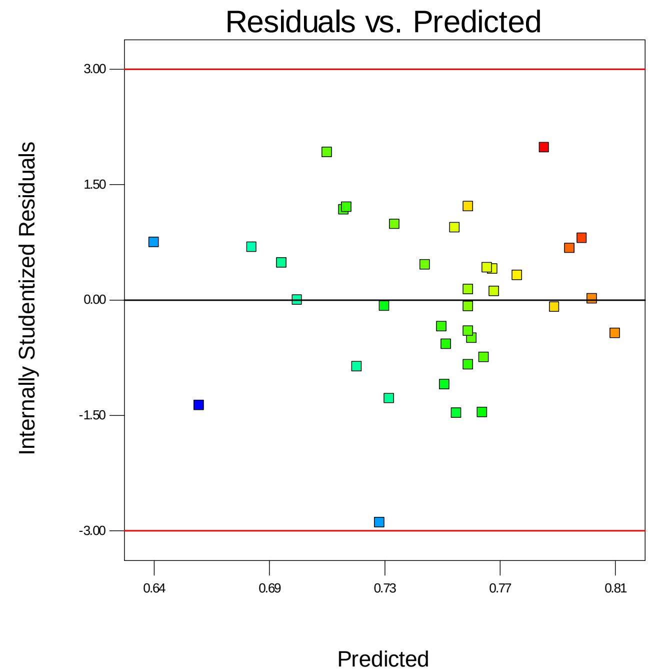
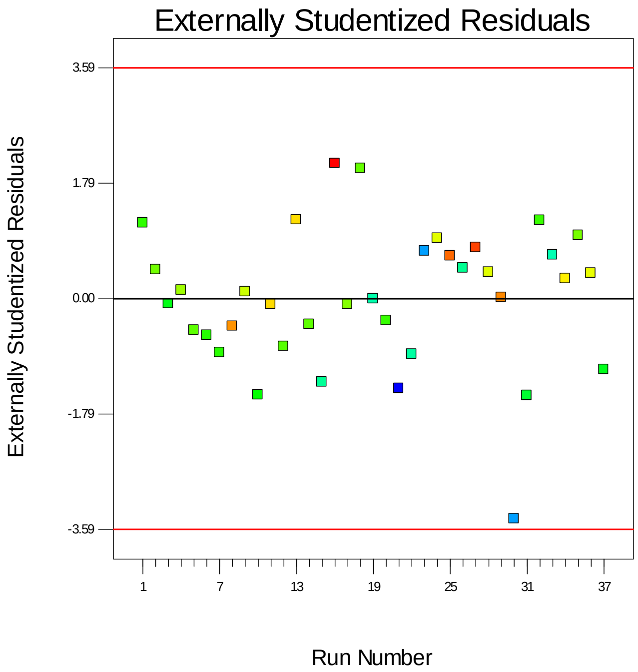


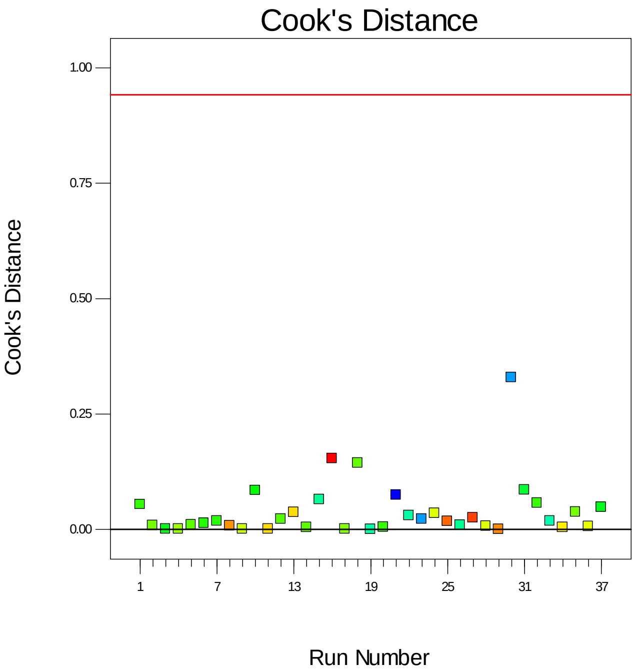
Figure C.14.2: Diagnostic Charts for the Tint Strength (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.



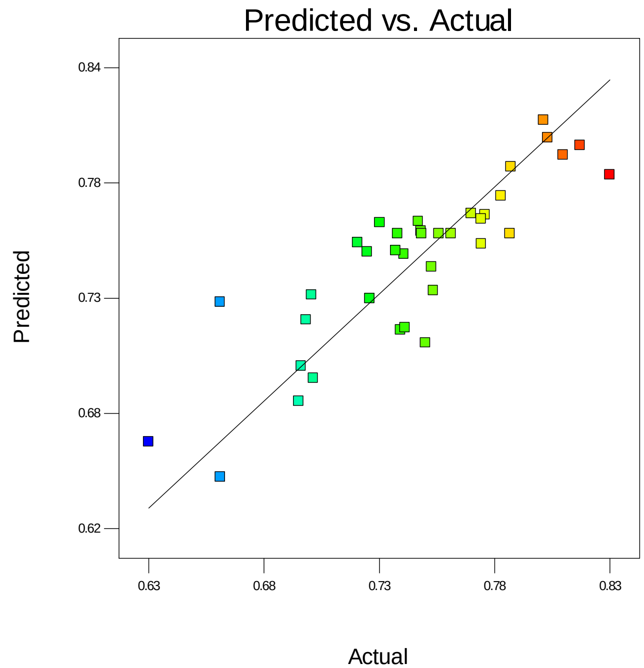




Externally Studentized Residuals
Externally Studentized Residuals
3.59
1.79
0.00
-1.79
-3.59
1
7
13
19
25
31
37
Run Number



Cook's Distance
Cook's Distance
1.00
0.75
0.50
0.25
0.00
1
7
13
19
25
31
37
Run Number


Predicted vs. Actual
Predicted
Actual
0.84
0.78
0.73
0.68
0.62
0.63
0.68
0.73
0.78
0.83

Appendix C.4 - Screening Phase ANOVA

Response **5 VMD**

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	7582.535097	7	1083.2193	14.0441	**< 0.0001**	**significant**
A-Polyester	2221.611153	1	2221.611153	28.8035	**< 0.0001**	
C-Styrene	796.5038281	1	796.5038281	10.3268	**0.0033**	
D-Lauryl Methacrylate	1358.116903	1	1358.116903	17.6082	**0.0002**	
E-DETA organic	2.065528125	1	2.065528125	0.02678	0.8712	
F-Water	2079.641278	1	2079.641278	26.9629	**< 0.0001**	
N-Stirrer speed	716.9737781	1	716.9737781	9.29568	**0.0050**	
AE	407.6226281	1	407.6226281	5.28489	**0.0292**	
Curvature	8.477946098	1	8.477946098	0.10992	0.7427	not significant
Residual	2159.63473	28	77.12981179			
Lack of Fit	2144.20725	24	89.34196875	23.1644	**0.0038**	**significant**
Pure Error	15.42748	4	3.85687			
Cor Total	9750.647773	36				

Std. Dev.	8.782357986	**R-Squared**	0.77832
Mean	41.80702703	**Adj R-Squared**	0.7229
C.V. %	21.00689432	**Pred R-Squared**	0.60659
PRESS	3836.029438	**Adeq Precision**	14.9497

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	41.6178125	1	1.552516222	38.4376	44.798	
A-Polyester	-8.3321875	1	1.552516222	-11.512	-5.152	1
C-Styrene	-4.9890625	1	1.552516222	-8.1692	-1.80888	1
D-Lauryl Methacrylate	6.5146875	1	1.552516222	3.3345	9.694873	1
E-DETA organic	-0.2540625	1	1.552516222	-3.4342	2.926123	1
F-Water	8.0615625	1	1.552516222	4.88138	11.24175	1
N-Stirrer speed	-4.7334375	1	1.552516222	-7.9136	-1.55325	1
AE	-3.5690625	1	1.552516222	-6.7492	-0.38888	1
Center Point	1.4001875	1	4.22330072	-7.2509	10.05123	1

Final Equation in Terms of Coded Factors:

VMD	=
41.6178125	
-8.3321875	* A
-4.9890625	* C
6.5146875	* D
-0.2540625	* E
8.0615625	* F
-4.7334375	* N
-3.5690625	* A * E

Final Equation in Terms of Actual Factors:

VMD	=
-138.5811458	
0.131513009	* Polyester
-0.119736542	* Styrene
1.055522926	* Lauryl Methacrylate
17.57765997	* DETA organic
0.054602827	* Water
-0.15778125	* Stirrer speed
-0.024474236	* Polyester * DETA organic

Response **1 Buildup**

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	98.4688	7	14.06696429	21.882	**< 0.0001**	**significant**
C-Styrene	42.7813	1	42.78125	66.549	**< 0.0001**	
D-Lauryl Methacrylate	3.78125	1	3.78125	5.8819	**0.0220**	
E-DETA organic	22.7813	1	22.78125	35.438	**< 0.0001**	
F-Water	7.03125	1	7.03125	10.938	**0.0026**	
L-Cumene hydroperoxide	7.03125	1	7.03125	10.938	**0.0026**	
M-Initial Reactor Temp.	11.2813	1	11.28125	17.549	**0.0003**	
N-Stirrer speed	3.78125	1	3.78125	5.8819	**0.0220**	
Curvature	7.09882	1	7.098817568	11.043	**0.0025**	**significant**
Residual	18	28	0.642857143			
Lack of Fit	16	24	0.666666667	1.3333	0.4323	not significant
Pure Error	2	4	0.5			
Cor Total	123.568	36				

Std. Dev.	0.80178	**R-Squared**	0.8455
Mean	2.10811	**Adj R-Squared**	0.8068
C.V. %	38.0333	**Pred R-Squared**	0.7445
PRESS	31.5694	**Adeq Precision**	16.596

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	2.28125	1	0.141736677	1.9909	2.571584	
C-Styrene	1.15625	1	0.141736677	0.8659	1.446584	1
D-Lauryl Methacrylate	0.34375	1	0.141736677	0.0534	0.634084	1
E-DETA organic	0.84375	1	0.141736677	0.5534	1.134084	1
F-Water	-0.4688	1	0.141736677	-0.759	-0.17842	1
L-Cumene hydroperoxide	-0.4688	1	0.141736677	-0.759	-0.17842	1
M-Initial Reactor Temp.	-0.5938	1	0.141736677	-0.884	-0.30342	1
N-Stirrer speed	0.34375	1	0.141736677	0.0534	0.634084	1
Center Point	-1.2813	1	0.385565447	-2.071	-0.49145	1

Final Equation in Terms of Coded Factors:

Buildup	=
2.28125	
1.15625	* C
0.34375	* D
0.84375	* E
-0.4688	* F
-0.4688	* L
-0.5938	* M
0.34375	* N

Final Equation in Terms of Actual Factors:

Buildup	=
-2.8646	
0.02775	* Styrene
0.0557	* Lauryl Methacrylate
0.41853	* DETA organic
-0.0032	* Water
-0.4069	* Cumene hydroperoxide
-0.0792	* Initial Reactor Temp.
0.01146	* Stirrer speed

Response **7 SDevV**

	Sum of		Mean	F	p-value	
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	2499.3	9	277.7002569	21.889	**< 0.0001**	**significant**
A-Polyester	835.587	1	835.5872	65.863	**< 0.0001**	
C-Styrene	117.275	1	117.2746125	9.2439	**0.0053**	
D-Lauryl Methacrylate	466.499	1	466.4985125	36.771	**< 0.0001**	
E-DETA organic	46.8512	1	46.8512	3.6929	0.0657	
F-Water	573.588	1	573.58845	45.212	**< 0.0001**	
G-PVOH	109.224	1	109.2242	8.6093	**0.0069**	
K-Ferrous sulphate	83.2695	1	83.2695125	6.5635	**0.0166**	
N-Stirrer speed	126.644	1	126.6436125	9.9824	**0.0040**	
AE	140.365	1	140.3650125	11.064	**0.0026**	
Curvature	0.94966	1	0.94966223	0.0749	0.7866	not significant
Residual	329.855	26	12.68672135			
Lack of Fit	327.825	22	14.90113068	29.364	**0.0024**	**significant**
Pure Error	2.02988	4	0.50747			
Cor Total	2830.11	36				

Std. Dev.	3.56184	**R-Squared**	0.8834
Mean	21.2027	**Adj R-Squared**	0.8431
C.V. %	16.799	**Pred R-Squared**	0.7538
PRESS	696.752	**Adeq Precision**	19.585

	Coefficient		Standard	95% CI	95% CI	
Factor	**Estimate**	**df**	**Error**	**Low**	**High**	**VIF**
Intercept	21.1394	1	0.62965073	19.845	22.43364	
A-Polyester	-5.11	1	0.62965073	-6.404	-3.815734	1
C-Styrene	-1.9144	1	0.62965073	-3.209	-0.620109	1
D-Lauryl Methacrylate	3.81813	1	0.62965073	2.5239	5.112391	1
E-DETA organic	1.21	1	0.62965073	-0.084	2.504266	1
F-Water	4.23375	1	0.62965073	2.9395	5.528016	1
G-PVOH	-1.8475	1	0.62965073	-3.142	-0.553234	1
K-Ferrous sulphate	1.61313	1	0.62965073	0.3189	2.907391	1
N-Stirrer speed	-1.9894	1	0.62965073	-3.284	-0.695109	1
AE	-2.0944	1	0.62965073	-3.389	-0.800109	1
Center Point	0.46863	1	1.712835168	-3.052	3.989408	1

Final Equation in Terms of Coded Factors:

SDevV	=
21.1394	
-5.11	* A
-1.9144	* C
3.81813	* D
1.21	* E
4.23375	* F
-1.8475	* G
1.61313	* K
-1.9894	* N
-2.0944	* A * E

Final Equation in Terms of Actual Factors:

SDevV	=
-85.117	
0.07412	* Polyester
-0.0459	* Styrene
0.61862	* Lauryl Methacrylate
10.989	* DETA organic
0.02868	* Water
-0.0294	* PVOH
16.8034	* Ferrous sulphate
-0.0663	* Stirrer speed
-0.0144	* Polyester * DETA organic

Response **19 CV (VMD)**

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	577.517	3	192.5056082	11.58	**< 0.0001**	**significant**
A-Polyester	110.871	1	110.8710105	6.6691	**0.0146**	
C-Styrene	100.298	1	100.2982642	6.0331	**0.0197**	
E-DETA organic	366.348	1	366.3475498	22.037	**< 0.0001**	
Curvature	3.02927	1	3.029269712	0.1822	0.6723	not significant
Residual	531.986	32	16.62456783			
Lack of Fit	525.671	28	18.77397969	11.892	**0.0134**	**significant**
Pure Error	6.31474	4	1.578684831			
Cor Total	1112.53	36				

Std. Dev.	4.07732	**R-Squared**	0.5205
Mean	50.9873	**Adj R-Squared**	0.4756
C.V. %	7.99674	**Pred R-Squared**	0.374
PRESS	696.458	**Adeq Precision**	9.3609

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	51.1004	1	0.720775794	49.632	52.5686	
A-Polyester	-1.86138	1	0.720775794	-3.33	-0.3932	1
C-Styrene	1.7704	1	0.720775794	0.3022	3.23857	1
E-DETA organic	3.38354	1	0.720775794	1.9154	4.85171	1
Center Point	-0.83697	1	1.96072214	-4.831	3.15689	1

Final Equation in Terms of Coded Factors:

CV (VMD) =
51.1004
-1.86138 * A
1.7704 * C
3.38354 * E

Final Equation in Terms of Actual Factors:

CV (VMD) =
40.9938
-0.02573 * Polyester
0.04249 * Styrene
1.67834 * DETA organic

Response **8 Brookfield**

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	9.3E+08	6	155440783.4	32.2	**< 0.0001**	**significant**
A-Polyester	2.4E+08	1	241124643	49.95	**< 0.0001**	
E-DETA organic	4.2E+08	1	418493424.5	86.69	**< 0.0001**	
G-PVOH	4.5E+07	1	44843527.8	9.289	**0.0049**	
M-Initial Reactor Temp.	4.6E+07	1	46309966.2	9.593	**0.0043**	
AE	1.5E+08	1	148840337.1	30.83	**< 0.0001**	
EG	3.3E+07	1	33032801.6	6.842	**0.0140**	
Curvature	2.2E+07	1	21910564.79	4.539	**0.0417**	**significant**
Residual	1.4E+08	29	4827593.058			
Lack of Fit	1.4E+08	25	5559771.147	22.11	**0.0041**	**significant**
Pure Error	1005920	4	251480			
Cor Total	1.1E+09	36				

Std. Dev.	2197.18	**R-Squared**	0.869
Mean	5361.78	**Adj R-Squared**	0.842
C.V. %	40.9786	**Pred R-Squared**	0.791
PRESS	2.3E+08	**Adeq Precision**	17.13

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	5665.96	1	388.409942	4872	6460.347	
A-Polyester	-2745.02	1	388.409942	-3539	-1950.63	1
E-DETA organic	3616.34	1	388.409942	2822	4410.728	1
G-PVOH	1183.79	1	388.409942	389.4	1978.178	1
M-Initial Reactor Temp.	-1202.99	1	388.409942	-1997	-408.603	1
AE	-2156.68	1	388.409942	-2951	-1362.29	1
EG	1016.01	1	388.409942	221.6	1810.397	1
Center Point	-2250.96	1	1056.589274	-4412	-89.9917	1

Final Equation in Terms of Coded Factors:

Brookfielc	=
5665.96	
-2745.02	* A
3616.34	* E
1183.79	* G
-1202.99	* M
-2156.68	* A * E
1016.01	* E * G

Final Equation in Terms of Actual Factors:

Brookfielc	=
-50227.9	
111.125	* Polyester
7451.9	* DETA organic
-62.0581	* PVOH
-160.399	* Initial Reactor Temp.
-14.7891	* Polyester * DETA organic
8.02709	* DETA organic * PVOH

Response **2 SG**

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.00265	20	0.000132611	14.17	**< 0.0001**	**significant**
A-Polyester	0.00042	1	0.000422678	45.18	**< 0.0001**	
C-Styrene	0.0003	1	0.000303195	32.41	**< 0.0001**	
D-Lauryl Methacrylate	0.00016	1	0.00015532	16.6	**0.0010**	
E-DETA organic	8E-05	1	7.96953E-05	8.518	**0.0106**	
G-PVOH	1.8E-05	1	1.81503E-05	1.94	0.1840	
H-HEC	9.8E-06	1	9.79031E-06	1.046	0.3225	
J-DETA aqeuos	0.0001	1	0.00010332	11.04	**0.0046**	
K-Ferrous sulphate	9.2E-05	1	9.21403E-05	9.849	**0.0068**	
L-Cumene hydroperoxide	5.2E-05	1	5.17653E-05	5.533	**0.0327**	
M-Initial Reactor Temp.	1.6E-06	1	1.57531E-06	0.168	0.6874	
N-Stirrer speed	0.00019	1	0.00019257	20.58	**0.0004**	
O-Addition Rate	0.0002	1	0.000197508	21.11	**0.0004**	
P-Emulsification time	8.8E-05	1	8.81128E-05	9.418	**0.0078**	
AC	0.00031	1	0.000310628	33.2	**< 0.0001**	
AE	8.4E-05	1	8.35278E-05	8.928	**0.0092**	
AG	6.4E-05	1	6.41278E-05	6.854	**0.0194**	
AH	0.00011	1	0.000110633	11.83	**0.0037**	
AJ	8.4E-05	1	8.41753E-05	8.997	**0.0090**	
AM	8.9E-05	1	8.87778E-05	9.489	**0.0076**	
AO	0.00019	1	0.000194538	20.79	**0.0004**	
Curvature	0.00017	1	0.000170239	18.2	**0.0007**	**significant**
Residual	0.00014	15	9.3557E-06			
Lack of Fit	0.00011	11	1.03603E-05	1.571	0.3528	not significant
Pure Error	2.6E-05	4	0.000006593			
Cor Total	0.00296	36				

Std. Dev.	0.00306	**R-Squared**	0.95
Mean	1.04271	**Adj R-Squared**	0.883
C.V. %	0.29334	**Pred R-Squared**	0.661
PRESS	0.00101	**Adeq Precision**	15.72

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	1.04187	1	0.000540708	1.041	1.043018	
A-Polyester	0.00363	1	0.000540708	0.002	0.004787	1
C-Styrene	-0.00308	1	0.000540708	-0.004	-0.00193	1
D-Lauryl Methacrylate	-0.0022	1	0.000540708	-0.003	-0.00105	1
E-DETA organic	-0.00158	1	0.000540708	-0.003	-0.00043	1
G-PVOH	0.00075	1	0.000540708	-4E-04	0.001906	1
H-HEC	-0.00055	1	0.000540708	-0.002	0.000599	1
J-DETA aqeuos	-0.0018	1	0.000540708	-0.003	-0.00064	1
K-Ferrous sulphate	-0.0017	1	0.000540708	-0.003	-0.00054	1
L-Cumene hydroperoxide	0.00127	1	0.000540708	1E-04	0.002424	1
M-Initial Reactor Temp.	-0.00022	1	0.000540708	-0.001	0.000931	1
N-Stirrer speed	-0.00245	1	0.000540708	-0.004	-0.0013	1
O-Addition Rate	-0.00248	1	0.000540708	-0.004	-0.00133	1
P-Emulsification time	0.00166	1	0.000540708	5E-04	0.002812	1
AC	0.00312	1	0.000540708	0.002	0.004268	1
AE	0.00162	1	0.000540708	5E-04	0.002768	1
AG	-0.00142	1	0.000540708	-0.003	-0.00026	1

AH	-0.00186	1	0.000540708	-0.003	-0.00071	1
AJ	0.00162	1	0.000540708	5E-04	0.002774	1
AM	-0.00167	1	0.000540708	-0.003	-0.00051	1
AO	-0.00247	1	0.000540708	-0.004	-0.00131	1
Center Point	0.00627	1	0.001470886	0.003	0.009409	1

Final Equation in Terms of Coded Factors:

SG	=
1.04187	
0.00363	* A
-0.00308	* C
-0.0022	* D
-0.00158	* E
0.00075	* G
-0.00055	* H
-0.0018	* J
-0.0017	* K
0.00127	* L
-0.00022	* M
-0.00245	* N
-0.00248	* O
0.00166	* P
0.00312	* A * C
0.00162	* A * E
-0.00142	* A * G
-0.00186	* A * H
0.00162	* A * J
-0.00167	* A * M
-0.00247	* A * O

Final Equation in Terms of Actual Factors:

SG	=
1.02371	
0.00013	* Polyester
-0.00082	* Styrene
-0.00036	* Lauryl Methacrylate
-0.0088	* DETA organic
0.00024	* PVOH
0.00036	* HEC
-0.03349	* DETA aqeuos
-0.01768	* Ferrous sulphate
0.0011	* Cumene hydroperoxide
0.00219	* Initial Reactor Temp.
-8.2E-05	* Stirrer speed
0.00443	* Addition Rate
0.00017	* Emulsification time
1E-06	* Polyester * Styrene
1.1E-05	* Polyester * DETA organic
-3.1E-07	* Polyester * PVOH
-5.2E-07	* Polyester * HEC
4.2E-05	* Polyester * DETA aqeuos
-3.1E-06	* Polyester * Initial Reactor Temp.
-6.8E-06	* Polyester * Addition Rate

Response **3 NVC**

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.0067	5	0.001339394	43.247	**< 0.0001**	**significant**
A-Polyester	0.00294	1	0.002942404	95.006	**< 0.0001**	
C-Styrene	0.00121	1	0.001213397	39.179	**< 0.0001**	
F-Water	0.00191	1	0.001908848	61.634	**< 0.0001**	
G-PVOH	0.00016	1	0.000162225	5.238	**0.0293**	
H-HEC	0.00047	1	0.000470094	15.179	**0.0005**	
Curvature	1.5E-05	1	1.51066E-05	0.4878	0.4903	not significant
Residual	0.00093	30	3.09708E-05			
Lack of Fit	0.00089	26	3.41946E-05	3.4141	0.1201	not significant
Pure Error	4E-05	4	1.00158E-05			
Cor Total	0.00764	36				

Std. Dev.	0.00557	**R-Squared**	0.8782
Mean	0.24891	**Adj R-Squared**	0.8579
C.V. %	2.23577	**Pred R-Squared**	0.8156
PRESS	0.00141	**Adeq Precision**	20.699

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	0.24866	1	0.000983787	0.2467	0.25067	
A-Polyester	0.00959	1	0.000983787	0.0076	0.011598	1
C-Styrene	0.00616	1	0.000983787	0.0041	0.008167	1
F-Water	-0.0077	1	0.000983787	-0.01	-0.00571	1
G-PVOH	-0.0023	1	0.000983787	-0.004	-0.00024	1
H-HEC	-0.0038	1	0.000983787	-0.006	-0.00182	1
Center Point	0.00187	1	0.002676191	-0.004	0.007335	1

Final Equation in Terms of Coded Factors:

NVC	=	
0.24866		
0.00959	*	A
0.00616	*	C
-0.0077	*	F
-0.0023	*	G
-0.0038	*	H

Final Equation in Terms of Actual Factors:

NVC	=	
0.30129		
0.00013	*	Polyester
0.00015	*	Styrene
-5E-05	*	Water
-4E-05	*	PVOH
-8E-05	*	HEC

Response **4 SMD**

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	3279.64	10	327.9641506	14.22	**< 0.0001**	**significant**
A-Polyester	227.218	1	227.2179031	9.851	**0.0043**	
C-Styrene	721.715	1	721.7150281	31.29	**< 0.0001**	
D-Lauryl Methacrylate	272.086	1	272.0861281	11.8	**0.0021**	
E-DETA organic	254.533	1	254.5332031	11.04	**0.0028**	
F-Water	736.608	1	736.6081531	31.94	**< 0.0001**	
H-HEC	212.953	1	212.9532031	9.233	**0.0055**	
M-Initial Reactor Temp.	31.502	1	31.50195313	1.366	0.2536	
N-Stirrer speed	378.331	1	378.3312781	16.4	**0.0004**	
P-Emulsification time	279.484	1	279.4839031	12.12	**0.0019**	
CM	165.211	1	165.2107531	7.163	**0.0129**	
Curvature	0.00086	1	0.000855152	4E-05	0.9952	not significant
Residual	576.629	25	23.06516263			
Lack of Fit	571.086	21	27.19457455	19.62	**0.0052**	**significant**
Pure Error	5.543	4	1.38575			
Cor Total	3856.27	36				

Std. Dev.	4.80262	**R-Squared**	0.85
Mean	23.8222	**Adj R-Squared**	0.791
C.V. %	20.1603	**Pred R-Squared**	0.654
PRESS	1334.72	**Adeq Precision**	16.15

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	23.8241	1	0.848991362	22.08	25.5726	
A-Polyester	-2.6647	1	0.848991362	-4.413	-0.91616	1
C-Styrene	-4.7491	1	0.848991362	-6.498	-3.00053	1
D-Lauryl Methacrylate	2.91594	1	0.848991362	1.167	4.66447	1
E-DETA organic	-2.8203	1	0.848991362	-4.569	-1.07178	1
F-Water	4.79781	1	0.848991362	3.049	6.54634	1
H-HEC	-2.5797	1	0.848991362	-4.328	-0.83116	1
M-Initial Reactor Temp.	0.99219	1	0.848991362	-0.756	2.74072	1
N-Stirrer speed	-3.4384	1	0.848991362	-5.187	-1.68991	1
P-Emulsification time	-2.9553	1	0.848991362	-4.704	-1.20678	1
CM	-2.2722	1	0.848991362	-4.021	-0.52366	1
Center Point	-0.0141	1	2.309506193	-4.771	4.74245	1

Final Equation in Terms of Coded Factors:

SMD	=
23.8241	
-2.6647	* A
-4.7491	* C
2.91594	* D
-2.8203	* E
4.79781	* F
-2.5797	* H
0.99219	* M
-3.4384	* N
-2.9553	* P
-2.2722	* C * M

Final Equation in Terms of Actual Factors:

SMD	=
19.3612	
-0.0368	* Polyester
0.04962	* Styrene
0.47245	* Lauryl Methacrylate
-1.399	* DETA organic
0.0325	* Water
-0.0522	* HEC
2.15201	* Initial Reactor Temp.
-0.1146	* Stirrer speed
-0.2955	* Emulsification time
-0.0073	* Styrene * Initial Reactor Temp.

Response **6 SDevS**

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	1752.23	7	250.3189857	15.37	**< 0.0001**	**significant**
A-Polyester	571.896	1	571.8962	35.11	**< 0.0001**	
C-Styrene	164.258	1	164.2578125	10.08	**0.0036**	
D-Lauryl Methacrylate	332.433	1	332.4331125	20.41	**0.0001**	
E-DETA organic	1.7672	1	1.7672	0.108	0.7443	
F-Water	466.04	1	466.04045	28.61	**< 0.0001**	
N-Stirrer speed	110.931	1	110.9305125	6.81	**0.0144**	
AE	104.908	1	104.9076125	6.44	**0.0170**	
Curvature	8.44694	1	8.446943311	0.519	0.4774	not significant
Residual	456.089	28	16.2888917			
Lack of Fit	451.989	24	18.83287865	18.37	**0.0059**	**significant**
Pure Error	4.09988	4	1.02497			
Cor Total	2216.77	36				

Std. Dev.	4.03595	**R-Squared**	0.793
Mean	20.1632	**Adj R-Squared**	0.742
C.V. %	20.0164	**Pred R-Squared**	0.635
PRESS	809.942	**Adeq Precision**	15.7

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	19.9744	1	0.713461888	18.51	21.4358	
A-Polyester	-4.2275	1	0.713461888	-5.69	-2.766	1
C-Styrene	-2.2656	1	0.713461888	-3.73	-0.8042	1
D-Lauryl Methacrylate	3.22313	1	0.713461888	1.762	4.68459	1
E-DETA organic	0.235	1	0.713461888	-1.23	1.69646	1
F-Water	3.81625	1	0.713461888	2.355	5.27771	1
N-Stirrer speed	-1.8619	1	0.713461888	-3.32	-0.4004	1
AE	-1.8106	1	0.713461888	-3.27	-0.3492	1
Center Point	1.39763	1	1.940826166	-2.58	5.37323	1

Final Equation in Terms of Coded Factors:

SDevS	=
19.9744	
-4.2275	* A
-2.2656	* C
3.22313	* D
0.235	* E
3.81625	* F
-1.8619	* N
-1.8106	* A * E

Final Equation in Terms of Actual Factors:

SDevS	=
-75.454	
0.06671	* Polyester
-0.0544	* Styrene
0.52222	* Lauryl Methacrylate
9.09784	* DETA organic
0.02585	* Water
-0.0621	* Stirrer speed
-0.0124	* Polyester * DETA organic

Response **18 CV (SMD)**

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	10129.8	9	1125.528547	13.63	**< 0.0001**	**significant**
A-Polyester	1954.14	1	1954.136433	23.67	**< 0.0001**	
B-Tioxide	831.068	1	831.0680546	10.07	**0.0039**	
C-Styrene	1455.14	1	1455.138257	17.63	**0.0003**	
D-Lauryl Methacrylate	220.013	1	220.0129353	2.665	0.1146	
E-DETA organic	2614.54	1	2614.536461	31.67	**< 0.0001**	
O-Addition Rate	575.329	1	575.3286953	6.969	**0.0138**	
P-Emulsification time	1233.78	1	1233.780438	14.95	**0.0007**	
AD	630.945	1	630.945337	7.643	**0.0103**	
AE	614.81	1	614.8103107	7.448	**0.0112**	
Curvature	21.4148	1	21.41481673	0.259	0.6148	not significant
Residual	2146.3	26	82.55018091			
Lack of Fit	2096.84	22	95.31077778	7.707	**0.0301**	**significant**
Pure Error	49.4676	4	12.3668981			
Cor Total	12297.5	36				

Std. Dev.	9.08571	**R-Squared**	0.825
Mean	87.8993	**Adj R-Squared**	0.765
C.V. %	10.3365	**Pred R-Squared**	0.633
PRESS	4513.58	**Adeq Precision**	13.84

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	87.5985	1	1.60614232	84.3	90.9	
A-Polyester	-7.8145	1	1.60614232	-11.12	-4.513	1
B-Tioxide	-5.0962	1	1.60614232	-8.398	-1.7947	1
C-Styrene	6.74337	1	1.60614232	3.442	10.0448	1
D-Lauryl Methacrylate	2.6221	1	1.60614232	-0.679	5.92357	1
E-DETA organic	9.03904	1	1.60614232	5.738	12.3405	1
O-Addition Rate	4.24017	1	1.60614232	0.939	7.54164	1
P-Emulsification time	6.20932	1	1.60614232	2.908	9.51079	1
AD	-4.4404	1	1.60614232	-7.742	-1.1389	1
AE	-4.3832	1	1.60614232	-7.685	-1.0818	1
Center Point	2.22535	1	4.369179481	-6.756	11.2063	1

Final Equation in Terms of Coded Factors:

CV (SMD)	=
87.5985	
-7.8145	* A
-5.0962	* B
6.74337	* C
2.6221	* D
9.03904	* E
4.24017	* O
6.20932	* P
-4.4404	* A * D
-4.3832	* A * E

Final Equation in Terms of Actual Factors:

CV (SMD)	=
-379.21	
0.50188	* Polyester
-0.4826	* Tioxide
0.16184	* Styrene
7.61924	* Lauryl Methacrylate
26.2259	* DETA organic
0.84803	* Addition Rate
0.62093	* Emulsification time
-0.0099	* Polyester * Lauryl Methacrylate
-0.0301	* Polyester * DETA organic

Response 9 **CR**

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.32795	3	0.109316881	9.069	**0.0002**	**significant**
E-DETA organic	0.07371	1	0.073708801	6.115	**0.0189**	
F-Water	0.07619	1	0.076186561	6.321	**0.0172**	
M-Initial Reactor Temp.	0.17806	1	0.178055281	14.77	**0.0005**	
Curvature	0.01337	1	0.013366841	1.109	0.3002	not significant
Residual	0.38571	32	0.012053477			
Lack of Fit	0.37746	28	0.01348081	6.537	**0.0399**	**significant**
Pure Error	0.00825	4	0.002062148			
Cor Total	0.72703	36				

Std. Dev.	0.10979	**R-Squared**	0.46
Mean	0.74868	**Adj R-Squared**	0.409
C.V. %	14.6643	**Pred R-Squared**	0.304
PRESS	0.5059	**Adeq Precision**	8.493

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	0.74116	1	0.019408018	0.702	0.780695	
E-DETA organic	0.04799	1	0.019408018	0.008	0.087527	1
F-Water	-0.0488	1	0.019408018	-0.088	-0.00926	1
M-Initial Reactor Temp.	-0.0746	1	0.019408018	-0.114	-0.03506	1
Center Point	0.0556	1	0.052795516	-0.052	0.163138	1

Final Equation in Terms of Coded Factors:

CR =
0.74116
0.04799 * E
-0.0488 * F
-0.0746 * M

Final Equation in Terms of Actual Factors:

CR =
1.5382
0.02381 * DETA organic
-0.0003 * Water
-0.0099 * Initial Reactor Temp.

Response **20 Coarseness**

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	53.125	3	17.70833333	15.71	**< 0.0001**	**significant**
A-Polyester	28.125	1	28.125	24.95	**< 0.0001**	
D-Lauryl Methacrylate	12.5	1	12.5	11.09	**0.0022**	
F-Water	12.5	1	12.5	11.09	**0.0022**	
Curvature	0.04324	1	0.043243243	0.038	0.8460	not significant
Residual	36.075	32	1.12734375			
Lack of Fit	34.875	28	1.245535714	4.152	0.0872	not significant
Pure Error	1.2	4	0.3			
Cor Total	89.2432	36				

Std. Dev.	1.06176	**R-Squared**	0.596
Mean	2.51351	**Adj R-Squared**	0.558
C.V. %	42.2422	**Pred R-Squared**	0.469
PRESS	47.426	**Adeq Precision**	11.21

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	2.5	1	0.187695211	2.118	2.88232	
A-Polyester	-0.9375	1	0.187695211	-1.32	-0.55518	1
D-Lauryl Methacrylate	0.625	1	0.187695211	0.243	1.00732	1
F-Water	0.625	1	0.187695211	0.243	1.00732	1
Center Point	0.1	1	0.510586175	-0.94	1.14003	1

Final Equation in Terms of Coded Factors:

Coarsene:	=
2.5	
-0.9375	* A
0.625	* D
0.625	* F

Final Equation in Terms of Actual Factors:

Coarsene:	=
-1.6667	
-0.013	* Polyester
0.10126	* Lauryl Methacrylate
0.00423	* Water

Response **21 TS ave**

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.05441	8	0.006800851	9.278	**< 0.0001**	**significant**
A-Polyester	0.0079	1	0.007900245	10.78	**0.0028**	
B-Tioxide	0.01049	1	0.010490761	14.31	**0.0008**	
E-DETA organic	0.01094	1	0.010937205	14.92	**0.0006**	
F-Water	0.00222	1	0.002221111	3.03	0.0931	
P-Emulsification time	0.0008	1	0.000802001	1.094	0.3048	
AE	0.00882	1	0.00881792	12.03	**0.0018**	
AF	0.0075	1	0.007497001	10.23	**0.0035**	
AP	0.00574	1	0.005740561	7.832	**0.0094**	
Curvature	0.001	1	0.001004687	1.371	0.2519	not significant
Residual	0.01979	27	0.000733008			
Lack of Fit	0.0184	23	0.000799973	2.299	0.2180	not significant
Pure Error	0.00139	4	0.000347957			
Cor Total	0.0752	36				

Std. Dev.	0.02707	**R-Squared**	0.733
Mean	0.7475	**Adj R-Squared**	0.654
C.V. %	3.62197	**Pred R-Squared**	0.497
PRESS	0.03779	**Adeq Precision**	12.11

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	0.74544	1	0.004786074	0.736	0.75526	
A-Polyester	0.01571	1	0.004786074	0.006	0.02553	1
B-Tioxide	0.01811	1	0.004786074	0.008	0.02793	1
E-DETA organic	-0.0185	1	0.004786074	-0.03	-0.00867	1
F-Water	-0.0083	1	0.004786074	-0.02	0.00149	1
P-Emulsification time	-0.005	1	0.004786074	-0.01	0.00481	1
AE	0.0166	1	0.004786074	0.007	0.02642	1
AF	0.01531	1	0.004786074	0.005	0.02513	1
AP	-0.0134	1	0.004786074	-0.02	-0.00357	1
Center Point	0.01524	1	0.013019528	-0.01	0.04196	1

Final Equation in Terms of Coded Factors:

TS ave	=
0.74544	
0.01571	* A
0.01811	* B
-0.0185	* E
-0.0083	* F
-0.005	* P
0.0166	* A * E
0.01531	* A * F
-0.0134	* A * P

Final Equation in Terms of Actual Factors:

TS ave	=
3.87036	
-0.0041	* Polyester
0.00171	* Tioxide
-0.0915	* DETA organic
-0.0011	* Water
0.01289	* Emulsification time
0.00011	* Polyester * DETA organic
1.4E-06	* Polyester * Water
-2E-05	* Polyester * Emulsification time

Appendix D: ANOVA Reference Guide*

1. Analysis of Variance (ANOVA) – A set of statistical methods for partitioning the variance into its components and then comparing the partitioned variances to determine if there is a statistically significant difference in the means.

2. Sum of Squares (SS) – Sum of the squared differences between the average source and the overall mean.

Total: $$\sum_{i=1}^{n}(y_i - \bar{y})^2 \tag{D.1}$$

Model: $$\sum_{i=1}^{n}(\hat{y}_i - \bar{y})^2 \tag{D.2}$$

3. Degrees of Freedom (df) – The number of variables which are free to vary. Generally calculated as: total variables minus one.

4. Mean Sum of Squares (MSS) – Estimate of the term variance calculated as the SS divided by df.

5. F-Value – Used to test for term significance by comparing the term variance to the residual variance. ($F = MSS_M/MSS_R$)

6. p-value – The probability that an F-value of this size was due to noise.

7. Curvature – Compares the average response of the factorial points to the average response of the centre points to test for non-linearity.

8. Lack of fit – Portion of the residual SS attributed to the model not fitting the data.

9. Residuals SS – Portion of the total SS that is not explained by the model.

$$\sum_{i=1}^{n}(y_i - \hat{y}_i)^2 \tag{D.3}$$

10. Pure error – Amount of variation in the response of replicated points.

11. Root MSE – The standard deviation associated with the experimental error. $\left(\sqrt{MSS_R}\right)$

12. Mean – Overall average of all the response data.

13. Coefficient of variance (C.V%) – The standard deviation expressed as a percentage of the mean. Useful for comparing the standard deviation, independent of the mean.

14. PRESS - Predicted Residual Error Sum of Squares.

15. R^2 – The coefficient of determination is a measure of the amount of variation explained by the model.

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* The reference guide is paraphrased from the Design Expert 7® Software Help (Stat-Ease, 2005).

$$R^2 = 1 - \frac{SS_R}{SS_T} \tag{D.4}$$

16. Adj R^2 – The coefficient of determination adjusted for the number of terms.

$$Adj\ R^2 = 1 - \frac{MSS_R}{MSS_T} \tag{D.5}$$

17. Pred R^2 – is a measure of the amount of variation in new data explained by the model. This should be within 0.20 of the Adj R^2 otherwise there may be a problem with the model.

$$Pred\ R^2 = 1 - \frac{PRESS}{MSS_T} \tag{D.6}$$

18. Adequate Precision – The signal to noise ratio; should be greater than 4 for adequate model discrimination.

19. Standard error – The standard deviation associated with the coefficient estimates.

20. 95% CI – The 95% confidence interval for the coefficients.

Nomenclature

Latin Variable	Description	Units
df	Degrees of freedom	-
MSS	Mean Sum of Squares	-
SS	Sum of Squares	-
y	Actual response value	-
$\bar{y}$	Overall mean response value	-
$\hat{y}$	Modelled response value	-

Subscript	Description	Subscript	Description
i	Generic Subscript	M	Modelled
R	Residual	T	Total

Appendix E: Response Surface Model Appendices

Appendix E.1: RPD Design, Results & Diagnostics

Table E.1: Uncoded Factor Levels for the RPD Design.

Coded Factor in DX7®		A	B	C	D	E	F	G	H	J	
Run Number	Std No.	Mass UPR	Mass Styrene	Mass LMA	Mass DETA (Organic)	Mass Water	Stirrer Speed	Initial Reactor Temperature	UPR Acid Value	UPR Viscosity	UPR Batch Reference
SCR - 201	71	263.28g	115.67g	13.64g	4.25g	1028.91g	350 rpm	22.5°C	24.65 mgKOH/g	2273 cP	A
SCR - 202	40	302.62g	98.32g	10.91g	5.10g	967.18g	300 rpm	15°C	24.65 mgKOH/g	2273 cP	A
SCR - 203	70	341.96g	133.02g	10.91g	5.10g	1090.65g	300 rpm	30°C	24.65 mgKOH/g	1880 cP	B
SCR - 204	43	263.28g	98.32g	10.91g	5.10g	1028.91g	400 rpm	30°C	24.65 mgKOH/g	1880 cP	B
SCR - 205	17	263.28g	133.02g	10.91g	5.10g	967.18g	400 rpm	30°C	47.84 mgKOH/g	2273 cP	D
SCR - 206	51	263.28g	133.02g	10.91g	5.10g	1090.65g	400 rpm	15°C	47.84 mgKOH/g	2273 cP	D
SCR - 207	66	341.96g	133.02g	10.91g	3.40g	1090.65g	300 rpm	15°C	47.84 mgKOH/g	1880 cP	C
SCR - 208	60	302.62g	98.32g	16.37g	3.40g	967.18g	400 rpm	15°C	24.65 mgKOH/g	1880 cP	B
SCR - 209	54	341.96g	133.02g	16.37g	5.10g	967.18g	350 rpm	15°C	47.84 mgKOH/g	1880 cP	C
SCR - 210	15	263.28g	133.02g	10.91g	3.40g	1090.65g	300 rpm	30°C	47.84 mgKOH/g	2273 cP	D
SCR - 211	64	263.28g	98.32g	13.64g	3.40g	967.18g	400 rpm	30°C	47.84 mgKOH/g	2273 cP	D
SCR - 212	74	341.96g	98.32g	10.91g	3.40g	1090.65g	300 rpm	30°C	24.65 mgKOH/g	1880 cP	B
SCR - 213	65	263.28g	133.02g	16.37g	5.10g	1090.65g	300 rpm	30°C	47.84 mgKOH/g	1880 cP	C
SCR - 214	49	341.96g	98.32g	10.91g	3.40g	967.18g	300 rpm	15°C	47.84 mgKOH/g	2273 cP	D
SCR - 215	10	341.96g	98.32g	10.91g	5.10g	1090.65g	300 rpm	15°C	47.84 mgKOH/g	2273 cP	D
SCR - 216	30	263.28g	98.32g	16.37g	5.10g	967.18g	400 rpm	22.5°C	47.84 mgKOH/g	1880 cP	C
SCR - 217	47	263.28g	133.02g	16.37g	3.40g	1028.91g	400 rpm	30°C	47.84 mgKOH/g	1880 cP	C
SCR - 218	55	341.96g	115.67g	10.91g	5.10g	967.18g	300 rpm	30°C	47.84 mgKOH/g	1880 cP	C
SCR - 219	63	341.96g	133.02g	16.37g	5.10g	1090.65g	300 rpm	30°C	24.65 mgKOH/g	2273 cP	A
SCR - 220	34	263.28g	133.02g	10.91g	5.10g	967.18g	300 rpm	15°C	47.84 mgKOH/g	1880 cP	C
SCR - 221	67	341.96g	133.02g	10.91g	3.40g	967.18g	300 rpm	15°C	24.65 mgKOH/g	1880 cP	B

Coded Factor in DX7®		A	B	C	D	E	F	G	H	J	
Run Number	Std No.	Mass UPR	Mass Styrene	Mass LMA	Mass DETA (Organic)	Mass Water	Stirrer Speed	Initial Reactor Temperature	UPR Acid Value	UPR Viscosity	UPR Batch Reference
SCR - 222	12	341.96g	98.32g	10.91g	3.40g	1090.65g	400 rpm	15°C	47.84 mgKOH/g	2273 cP	D
SCR - 223	24	341.96g	133.02g	16.37g	3.40g	1028.91g	300 rpm	30°C	24.65 mgKOH/g	1880 cP	B
SCR - 224	5	263.28g	133.02g	10.91g	5.10g	1090.65g	300 rpm	30°C	24.65 mgKOH/g	2273 cP	A
SCR - 225	61	263.28g	98.32g	10.91g	5.10g	1028.91g	300 rpm	30°C	47.84 mgKOH/g	2273 cP	D
SCR - 226	8	263.28g	133.02g	10.91g	3.40g	1090.65g	400 rpm	30°C	24.65 mgKOH/g	2273 cP	A
SCR - 227	42	263.28g	133.02g	10.91g	3.40g	967.18g	300 rpm	30°C	24.65 mgKOH/g	2273 cP	A
SCR - 228	4	341.96g	133.02g	16.37g	5.10g	967.18g	300 rpm	15°C	24.65 mgKOH/g	2273 cP	A
SCR - 229	28	341.96g	98.32g	13.64g	3.40g	967.18g	300 rpm	30°C	24.65 mgKOH/g	2273 cP	A
SCR - 230	29	263.28g	115.67g	16.37g	3.40g	1090.65g	300 rpm	15°C	47.84 mgKOH/g	1880 cP	C
SCR - 231	9	263.28g	133.02g	16.37g	5.10g	967.18g	300 rpm	15°C	47.84 mgKOH/g	2273 cP	D
SCR - 232	45	263.28g	98.32g	16.37g	5.10g	967.18g	300 rpm	15°C	24.65 mgKOH/g	2273 cP	A
SCR - 233	21	341.96g	133.02g	16.37g	3.40g	1090.65g	400 rpm	15°C	47.84 mgKOH/g	2273 cP	D
SCR - 234	33	341.96g	133.02g	10.91g	5.10g	1090.65g	400 rpm	22.5°C	47.84 mgKOH/g	1880 cP	C
SCR - 235	25	341.96g	133.02g	16.37g	3.40g	967.18g	300 rpm	22.5°C	47.84 mgKOH/g	1880 cP	C
SCR - 236	72	263.28g	133.02g	16.37g	5.10g	967.18g	300 rpm	15°C	47.84 mgKOH/g	2273 cP	D
SCR - 237	39	302.62g	133.02g	10.91g	3.40g	967.18g	400 rpm	15°C	47.84 mgKOH/g	1880 cP	C
SCR - 238	31	341.96g	98.32g	10.91g	3.40g	1090.65g	300 rpm	30°C	47.84 mgKOH/g	1880 cP	C
SCR - 239	68	263.28g	133.02g	16.37g	3.40g	967.18g	300 rpm	15°C	24.65 mgKOH/g	1880 cP	B
SCR - 240	73	263.28g	133.02g	10.91g	5.10g	967.18g	300 rpm	15°C	47.84 mgKOH/g	1880 cP	C
SCR - 241	20	341.96g	133.02g	16.37g	5.10g	1090.65g	400 rpm	30°C	24.65 mgKOH/g	1880 cP	B
SCR - 242	2	263.28g	133.02g	16.37g	5.10g	1090.65g	400 rpm	15°C	24.65 mgKOH/g	1880 cP	B
SCR - 243	38	341.96g	98.32g	16.37g	3.40g	1090.65g	350 rpm	15°C	24.65 mgKOH/g	2273 cP	A
SCR - 244	7	263.28g	98.32g	16.37g	5.10g	967.18g	400 rpm	30°C	24.65 mgKOH/g	2273 cP	A
SCR - 245	35	341.96g	133.02g	10.91g	5.10g	1028.91g	400 rpm	15°C	24.65 mgKOH/g	2273 cP	A
SCR - 246	23	341.96g	133.02g	13.64g	3.40g	1090.647	400 rpm	15°C	24.65 mgKOH/g	1880 cP	B
SCR - 247	27	263.28g	115.67g	13.64g	4.25g	1028.91g	350 rpm	22.5°C	24.65 mgKOH/g	2273 cP	A
SCR - 248	6	263.28g	133.02g	16.37g	3.40g	967.18g	400 rpm	30°C	24.65 mgKOH/g	2273 cP	A

Coded Factor in DX7®		A	B	C	D	E	F	G	H	J	
Run Number	Std No.	Mass UPR	Mass Styrene	Mass LMA	Mass DETA (Organic)	Mass Water	Stirrer Speed	Initial Reactor Temperature	UPR Acid Value	UPR Viscosity	UPR Batch Reference
SCR - 249	41	263.28g	98.32g	16.37g	3.40g	1090.65g	400 rpm	30°C	24.65 mgKOH/g	1880 cP	B
SCR - 250	44	341.96g	98.32g	10.91g	4.25g	967.18g	400 rpm	30°C	47.84 mgKOH/g	1880 cP	C
SCR - 251	18	341.96g	98.32g	10.91g	5.10g	1090.65g	400 rpm	30°C	47.84 mgKOH/g	2273 cP	D
SCR - 252	16	341.96g	133.02g	10.91g	3.40g	967.18g	400 rpm	30°C	47.84 mgKOH/g	2273 cP	D
SCR - 253	59	341.96g	98.32g	10.91g	5.10g	1090.65g	350 rpm	15°C	24.65 mgKOH/g	1880 cP	B
SCR - 254	36	341.96g	98.32g	10.91g	3.40g	967.18g	400 rpm	22.5°C	24.65 mgKOH/g	1880 cP	B
SCR - 255	46	341.96g	133.019	16.37g	5.10g	967.18g	400 rpm	30°C	47.84 mgKOH/g	2273 cP	D
SCR - 256	69	263.28g	98.32g	10.91g	3.40g	1090.65g	400 rpm	15°C	24.65 mgKOH/g	1880 cP	B
SCR - 257	19	263.28g	98.32g	16.37g	5.10g	1090.65g	400 rpm	30°C	47.84 mgKOH/g	2273 cP	D
SCR - 258	37	263.28g	98.32g	10.91g	5.10g	1090.65g	350 rpm	15°C	47.84 mgKOH/g	1880 cP	C
SCR - 259	13	263.28g	98.32g	16.37g	3.40g	1090.65g	400 rpm	15°C	47.84 mgKOH/g	2273 cP	D
SCR - 260	53	263.28g	98.32g	16.37g	3.40g	967.18g	300 rpm	30°C	47.84 mgKOH/g	1880 cP	C
SCR - 261	14	341.96g	98.32g	16.37g	5.10g	967.18g	300 rpm	30°C	47.84 mgKOH/g	2273 cP	D
SCR - 262	75	263.28g	98.32g	16.37g	5.10g	967.18g	400 rpm	22.5°C	47.84 mgKOH/g	1880 cP	C
SCR - 263	58	341.96g	98.32g	10.91g	4.25g	1090.65g	300 rpm	30°C	24.65 mgKOH/g	2273 cP	A
SCR - 264	32	263.28g	115.669	10.91g	3.40g	1090.65g	300 rpm	15°C	24.65 mgKOH/g	2273 cP	A
SCR - 265	26	341.96g	133.019	16.37g	3.40g	967.18g	300 rpm	15°C	24.65 mgKOH/g	2273 cP	A
SCR - 266	57	341.96g	98.32g	16.37g	4.25g	1090.65g	400 rpm	15°C	47.84 mgKOH/g	1880 cP	C
SCR - 267	22	302.62g	133.019	16.37g	5.10g	1090.65g	300 rpm	15°C	24.65 mgKOH/g	1880 cP	B
SCR - 268	52	263.28g	133.019	13.64g	5.10g	967.18g	400 rpm	30°C	24.65 mgKOH/g	1880 cP	B
SCR - 269	56	263.28g	98.32g	13.64g	5.10g	1090.65g	400 rpm	15°C	24.65 mgKOH/g	2273 cP	A
SCR - 270	1	263.28g	98.32g	10.91g	3.40g	967.18g	300 rpm	15°C	24.65 mgKOH/g	1880 cP	B
SCR - 271	50	263.28g	133.019	10.91g	3.40g	967.18g	350 rpm	15°C	24.65 mgKOH/g	2273 cP	A
SCR - 272	62	341.96g	115.669	16.37g	3.40g	1090.65g	300 rpm	30°C	47.84 mgKOH/g	2273 cP	D
SCR - 273	3	341.96g	98.32g	16.37g	5.10g	1090.65g	300 rpm	30°C	24.65 mgKOH/g	1880 cP	B
SCR - 274	11	341.96g	98.32g	10.91g	5.10g	967.18g	400 rpm	15°C	47.84 mgKOH/g	2273 cP	D
SCR - 275	48	263.28g	133.019	10.91g	4.25g	1090.65g	300 rpm	30°C	47.84 mgKOH/g	1880 cP	C

Table E.2: Response Results for the RPD Design

Run Number	Std No.	Buildup	SG	%NVC	SMD	VMD	SDevS	SDevV	CV (SMD)	CV (VMD)	Viscosity	CR	pH	Cost /kg
SCR - 201	71	0	1.0469	24.59%	21.99 µm	50.69 µm	25.12 µm	30.33 µm	114.23%	59.83%	1640cP	70.17%	8.66	R 5.08
SCR - 202	40	0	1.0504	25.63%	19.79 µm	35.11 µm	17.41 µm	18.30 µm	87.97%	52.12%	1548 cP	88.29%	8.38	R 5.38
SCR - 203	70	0	1.0510	27.02%	15.12 µm	25.12 µm	12.295 µm	11.37 µm	81.32%	45.27%	867.8 cP	86.52%	8.67	R 5.42
SCR - 204	43	0	1.0468	23.14%	21.55 µm	45.80 µm	21.90 µm	22.91 µm	101.62%	50.02%	2200 cP	85.01%	8.97	R 4.93
SCR - 205	17	4	1.0530	24.88%	13.03 µm	33.40 µm	16.29 µm	21.90 µm	125.02%	65.57%	1920 cP	73.65%	8.42	R 5.20
SCR - 206	51	2	1.0431	22.24%	23.74 µm	58.88 µm	28.88 µm	34.77 µm	121.65%	59.05%	2000 cP	76.48%	8.21	R 4.89
SCR - 207	66	0	1.0468	25.28%	8.77 µm	35.08 µm	15.19 µm	22.83 µm	173.20%	65.08%	703.8 cP	35.06%	8.18	R 5.39
SCR - 208	60	1	1.0520	26.03%	18.24 µm	31.96 µm	15.82 µm	16.60 µm	86.73%	51.94%	2060 cP	90.99%	8.61	R 5.58
SCR - 209	54	5	1.0545	28.07%	11.55 µm	25.10 µm	12.51 µm	12.71 µm	108.31%	50.64%	1120 cP	63.01%	7.7	R 5.97
SCR - 210	15	0	1.0405	22.64%	22.31 µm	60.61 µm	29.23 µm	30.50 µm	131.02%	50.32%	1376 cP	43.97%	7.8	R 4.86
SCR - 211	64	0	1.0477	22.95%	18.66 µm	46.89 µm	22.95 µm	22.57 µm	122.99%	48.13%	1456 cP	55.75%	7.81	R 5.18
SCR - 212	74	0	1.0523	26.06%	25.36 µm	37.21 µm	17.33 µm	17.67 µm	68.34%	47.49%	363.9 cP	80.99%	8.7	R 5.30
SCR - 213	65	2	1.0429	24.29%	13.20 µm	30.73 µm	15.21 µm	19.49 µm	115.23%	63.42%	1240 cP	48.13%	8.33	R 5.10
SCR - 214	49	0	1.0493	25.51%	23.74 µm	67.36 µm	32.18 µm	32.75 µm	135.55%	48.62%	583.9 cP	42.56%	7.86	R 5.63
SCR - 215	10	1	1.0523	25.17%	32.87 µm	77.74 µm	38.40 µm	43.16 µm	116.82%	55.52%	455.9 cP	50.82%	8.01	R 5.33
SCR - 216	30	2	1.0324	24.32%	11.54 µm	22.23 µm	11.10 µm	14.27 µm	96.19%	64.19%	743.8 cP	69.13%	8.21	R 5.33
SCR - 217	47	3	1.0443	23.40%	8.87 µm	23.78 µm	11.50 µm	14.50 µm	129.65%	60.98%	9078 cP	50.84%	7.98	R 5.23
SCR - 218	55	1	1.0536	27.19%	13.70 µm	26.35 µm	13.16 µm	12.68 µm	96.06%	48.12%	927.8 cP	46.30%	7.94	R 5.71
SCR - 219	63	1	1.0432	26.90%	26.22 µm	60.40 µm	29.94 µm	42.55 µm	114.19%	70.45%	627.9 cP	81.45%	8.04	R 5.63
SCR - 220	34	3	1.0451	24.87%	11.06 µm	21.01 µm	10.49 µm	11.35 µm	94.85%	54.02%	747.8 cP	63.14%	8.61	R 5.20
SCR - 221	67	1	1.0545	28.62%	13.05 µm	21.64 µm	10.59 µm	9.37 µm	81.15%	43.30%	1228 cP	86.50%	8.21	R 5.73
SCR - 222	12	0	1.0513	24.32%	22.68 µm	66.18 µm	31.41 µm	34.27 µm	138.49%	51.78%	567.9 cP	41.55%	7.68	R 5.30
SCR - 223	24	1	1.0513	27.73%	18.07 µm	31.12 µm	15.36 µm	14.33 µm	85.00%	46.05%	875.8 cP	76.48%	8.04	R 5.77
SCR - 224	5	0	1.0448	24.22%	24.74 µm	64.64 µm	31.42 µm	45.98 µm	127.00%	71.13%	4319 cP	68.41%	8.89	R 4.89
SCR - 225	61	0	1.0400	22.85%	35.63 µm	72.09 µm	36.04 µm	38.41 µm	101.15%	53.28%	1128 cP	64.30%	8.22	R 4.93
SCR - 226	8	0	1.0434	23.42%	13.09 µm	28.14 µm	14.03 µm	17.58 µm	107.18%	62.47%	491.9 cP	66.54%	8.76	R 4.86
SCR - 227	42	1	1.0471	25.55%	16.09 µm	31.38 µm	15.69 µm	17.00 µm	97.51%	54.17%	731.8 cP	69.19%	8.21	R 5.17
SCR - 228	4	1	1.0555	28.95%	22.98 µm	43.77 µm	21.86 µm	21.59 µm	95.13%	49.33%	1664 cP	86.38%	8.03	R 5.97
SCR - 229	28	0	1.0529	27.44%	31.03 µm	45.40 µm	21.12 µm	18.66 µm	68.06%	41.10%	619.9 cP	72.65%	8.14	R 5.74
SCR - 230	29	0	1.0346	22.04%	20.05 µm	44.03 µm	21.93 µm	20.98 µm	109.38%	47.65%	583.9 cP	49.53%	8.1	R 5.02
SCR - 231	9	3	1.0492	25.42%	16.85 µm	52.22 µm	24.41 µm	33.23 µm	144.87%	63.63%	3899 cP	71.91%	8.03	R 5.43
SCR - 232	45	5	-	23.84%	26.27 µm	44.27 µm	21.75 µm	18.39 µm	82.79%	41.54%	-	91.00%	7.69	R 5.33

Run Number	Std No.	Buildup	SG	%NVC	SMD	VMD	SDevS	SDevV	CV (SMD)	CV (VMD)	Viscosity	CR	pH	Cost /kg
SCR - 233	21	0	1.0489	25.17%	13.10 µm	61.07 µm	25.07 µm	36.41 µm	191.37%	59.62%	835.8 cP	40.47%	7.61	R 5.60
SCR - 234	33	5	1.0508	25.88%	9.81 µm	20.34 µm	10.17 µm	10.18 µm	103.67%	50.05%	847.8 cP	65.49%	7.82	R 5.42
SCR - 235	25	1	1.0534	27.00%	7.74 µm	32.99 µm	13.98 µm	23.02 µm	180.62%	69.78%	963.8 cP	39.10%	7.81	R 5.95
SCR - 236	72	2	1.0477	24.86%	21.20 µm	63.64 µm	29.99 µm	37.32 µm	141.46%	58.64%	4799 cP	74.58%	8.26	R 5.43
SCR - 237	39	2	1.0461	26.09%	7.46 µm	19.58 µm	9.51 µm	11.01 µm	127.48%	56.23%	731.8 cP	40.60%	8.61	R 5.45
SCR - 238	31	0	1.0464	25.44%	11.45 µm	49.61 µm	20.90 µm	27.25 µm	182.53%	54.93%	771.8 cP	35.32%	7.81	R 5.30
SCR - 239	68	1	1.0448	25.36%	20.57 µm	42.55 µm	21.67 µm	22.57 µm	105.35%	53.04%	7898 cP	93.40%	8.23	R 5.40
SCR - 240	73	3	1.0456	24.70%	11.46 µm	24.13 µm	12.05 µm	14.91 µm	105.15%	61.79%	703.8 cP	59.16%	8.04	R 5.20
SCR - 241	20	4	1.0492	26.55%	10.85 µm	20.76 µm	10.37 µm	11.82 µm	95.58%	56.94%	1464 cP	89.72%	8.31	R 5.63
SCR - 242	2	2	1.0250	23.51%	20.99 µm	51.80 µm	25.43 µm	30.51 µm	121.15%	58.90%	-	89.52%	8.06	R 5.10
SCR - 243	38	1	1.0412	25.50%	31.73 µm	58.57 µm	29.19 µm	31.60 µm	91.99%	53.95%	343.9 cP	74.59%	8.12	R 5.51
SCR - 244	7	0	1.0408	24.28%	17.95 µm	39.25 µm	19.55 µm	21.34 µm	108.91%	54.37%	1308 cP	78.11%	7.88	R 5.33
SCR - 245	35	0	1.0524	27.07%	10.99 µm	21.30 µm	10.65 µm	11.32 µm	96.91%	53.15%	515.9 cP	85.18%	7.68	R 5.58
SCR - 246	23	3	1.0500	26.12%	13.06 µm	21.56 µm	10.54 µm	9.68 µm	80.70%	44.90%	959.8 cP	90.74%	8.04	R 5.50
SCR - 247	27	0	1.0461	23.61%	20.42 µm	48.17 µm	23.80 µm	28.70 µm	116.55%	59.58%	967.8 cP	83.02%	8.11	R 5.08
SCR - 248	6	2	1.0474	25.55%	14.65 µm	35.27 µm	16.51 µm	20.56 µm	112.70%	58.29%	1560 cP	80.86%	8.64	R 5.40
SCR - 249	41	0	1.0394	22.68%	21.47 µm	48.79 µm	24.22 µm	26.99 µm	112.81%	55.32%	895.8 cP	81.16%	7.96	R 4.97
SCR - 250	44	2	1.0390	26.23%	12.24 µm	26.52 µm	13.22 µm	13.43 µm	108.01%	50.64%	891.8 cP	53.57%	8.06	R 5.65
SCR - 251	18	0	1.0489	24.68%	24.90 µm	48.55 µm	24.27 µm	21.95 µm	97.47%	45.21%	755.8 cP	62.54%	8.21	R 5.33
SCR - 252	16	4	1.0473	-	8.31 µm	29.69 µm	13.33 µm	19.65 µm	160.41%	66.18%	1320 cP	66.33%	8.04	R 5.73
SCR - 253	59	1	1.0495	25.34%	10.35 µm	17.06 µm	8.33 µm	7.98 µm	80.48%	46.78%	4339 cP	97.12%	8.08	R 5.33
SCR - 254	36	0	1.0494	27.13%	11.89 µm	19.16 µm	9.30 µm	8.43 µm	78.22%	44.00%	651.4 cP	90.78%	8.72	R 5.63
SCR - 255	46	4	1.033	28.07%	11.45 µm	36.40 µm	16.90 µm	20.24 µm	147.60%	55.60%	1796 cP	77.83%	8.04	R 5.97
SCR - 256	69	1	1.0378	22.72%	18.15 µm	35.48 µm	17.73 µm	18.82 µm	97.69%	53.04%	1572 cP	94.54%	7.96	R 4.75
SCR - 257	19	0	1.0264	21.99%	26.34 µm	71.00 µm	34.30 µm	45.31 µm	130.22%	63.82%	1456 cP	68.68%	8.12	R 5.00
SCR - 258	37	0	1.0431	22.40%	14.73 µm	33.32 µm	16.55 µm	21.71 µm	112.36%	65.16%	291.9 cP	62.66%	8.21	R 4.78
SCR - 259	13	0	1.0359	20.96%	20.30 µm	56.13 µm	26.97 µm	35.25 µm	132.86%	62.80%	539.9 cP	62.49%	7.96	R 4.97
SCR - 260	53	0	1.0400	23.55%	16.27 µm	49.40 µm	23.22 µm	28.03 µm	142.72%	56.74%	838.8 cP	41.11%	8.19	R 5.30
SCR - 261	14	0	1.0561	27.06%	35.45 µm	79.27 µm	39.41 µm	40.51 µm	111.17%	51.10%	1328 cP	56.05%	8.18	R 5.88
SCR - 262	75	2	1.0348	23.55%	11.96 µm	25.22 µm	12.59 µm	16.21 µm	105.27%	64.27%	663.9 cP	66.53%	8.21	R 5.33
SCR - 263	58	0	1.0423	25.34%	25.83 µm	45.60 µm	22.60 µm	20.00 µm	87.50%	43.86%	295.9 cP	60.99%	8.42	R 5.31
SCR - 264	32	1	1.0392	22.87%	28.27 µm	58.60 µm	29.28 µm	32.26 µm	103.57%	55.05%	487.9 cP	70.90%	7.96	R 4.81
SCR - 265	26	1	1.0550	28.53%	23.88 µm	39.77 µm	19.48 µm	17.16 µm	81.57%	43.15%	1724 cP	84.61%	8.14	R 5.95
SCR - 266	57	0	1.0496	24.64%	17.51 µm	46.62 µm	22.58 µm	23.78 µm	128.95%	51.01%	511.9 cP	58.44%	8.12	R 5.52

Run Number	Std No.	Buildup	SG	%NVC	SMD	VMD	SDevS	SDevV	CV (SMD)	CV (VMD)	Viscosity	CR	pH	Cost /kg
SCR - 267	22	5	-	25.80%	26.82 µm	54.91 µm	27.45 µm	28.38 µm	102.35%	51.68%	13877 cP	90.43%	7.98	R 5.37
SCR - 268	52	5	1.0443	25.22%	13.86 µm	34.05 µm	16.73 µm	19.86 µm	120.71%	58.33%	5679 cP	89.63%	8.31	R 5.32
SCR - 269	56	4	1.0316	22.17%	18.61 µm	34.08 µm	16.97 µm	16.76 µm	91.19%	49.18%	15477 cP	94.19%	7.96	R 4.89
SCR - 270	1	1	1.0431	23.70%	19.70 µm	34.13 µm	16.86 µm	16.85 µm	85.58%	49.37%	2132 cP	92.65%	8.12	R 5.06
SCR - 271	50	1	1.0363	24.62%	18.01 µm	35.26 µm	17.63 µm	18.27 µm	97.89%	51.82%	739.8 cP	79.92%	8.21	R 5.17
SCR - 272	62	0	1.0490	24.47%	17.46 µm	70.46 µm	30.41 µm	35.83 µm	174.17%	50.85%	1060 cP	43.78%	8.36	R 5.56
SCR - 273	3	0	1.0467	25.13%	29.19 µm	54.67 µm	27.27 µm	25.92 µm	93.42%	47.41%	767.3 cP	73.03%	8.67	R 5.54
SCR - 274	11	0	1.0491	26.22%	22.70 µm	48.30 µm	24.11 µm	26.17 µm	106.21%	54.18%	787.8 cP	70.40%	8.11	R 5.66
SCR - 275	48	1	1.0386	22.87%	12.99 µm	31.05 µm	15.32 µm	18.01 µm	117.94%	58.00%	599.9 cP	46.21%	8.14	R 4.87

Table E.3: Percentage Effects Contribution* for All Responses

Factor / Response	A: Mass UPR		B: Mass Styrene		C: Mass LMA		D: Mass DETA (Organic)		E: Mass Water		F: Stirrer Speed		G: Initial Temperature		H: Acid Value		J: Viscosity		2-factor interaction	Error
	A	A^2	B	B^2	C	C^2	D	D^2	E	E^2	F	F^2	G	G^2	H	H^2	J	J^2		
VMD /µm	2.34%		6.42%		7.17%		0.00%		9.08%		13.50%		0.00%		4.33%		23.28%		AB: 1.23% AC: 0.78% AD: 0.09% AE: 0.37% AG: 0.86% AH: 4.30% BD: 0.99% BG: 3.28% BH: 1.50% CH: 0.84% DG: 0.46% DH: 0.58% DJ: 0.50% EG: 0.44% EJ: 0.63% FJ: 1.31% GH: 0.51% HJ: 9.20%	6.02%
ln(Buildup+0.05)	0.19%		19.61%		1.65%		2.76%		2.37%		0.16%		2.07%		0.01%		3.77%		AE: 2.19% BE: 1.78% BG: 4.87% BH: 2.58% CD: 3.42% CH: 3.53% DE: 1.50% DH: 4.11% EG: 3.10% EH: 1.86% EJ: 1.71% FJ: 1.91% GH: 6.01% GJ: 1.99%	13.43%
SG /kg.dm^{-3}	30.80%				2.06%		0.01%		10.51%		3.94%		0.23%		0.64%		0.19%		AG: 3.55% AJ: 2.25% CD: 3.33% CE: 1.97% CF: 3.75% DF: 4.00% EF: 1.52% EH: 1.55% GH: 2.66%	27.03%
%NVC	58.93%		8.97%				0.87%		21.33%		0.36%		0.24%		4.73%		0.22%			4.35%
1/sqr(Viscosity)	10.09%		7.78%		6.25%	0.6 6%	8.47%		3.69%		0.03%		0.02%	1.33%	0.99%		1.78%		AB: 0.76% AC: 0.98% AD: 1.02% AH: 5.77% AJ: 2.17% BC: 0.88% BH: 2.12% CE: 0.85% DE: 0.93% DH: 6.50% EF: 1.50% FH: 0.95% FJ: 1.15% GH: 12.26% HJ: 9.43%	11.64%
CR	0.25%		0.08%		0.02%		7.71%		1.11%		4.14%		2.72%		64.95%		0.05%		AB: 0.65% AG: 1.42% AH: 1.29% BG: 1.03% CG: 0.39% DG: 0.37% DH: 2.45% DJ: 0.28% EJ: 0.47% FG: 0.37% GH: 0.90% HJ: 4.78%	4.55%
Cost /kg	64.91%		2.12%		9.93%		0.17%		22.82%											0.04%
SMD /µm	1.56%		17.75%		3.54%		0.93%		5.07%		14.99%		0.00%		3.83%		16.56%		AB: 1.95% AC: 0.80% AD: 0.70% AE: 1.64% BG: 3.76% BJ: 0.98% CH: 3.34% DG: 1.07% DH: 1.28% EG: 0.93% FH: 1.75% FJ: 1.96% HJ: 4.77%	10.83%

* The percentage effect contribution is sum of squares (see ANOVA) of the effect as a percentage of the total sum of squares for all the effects. The percentage effect contribution is only comparable if the effect terms have the same degrees of freedom.

Response \ Factor	A: Mass UPR		B: Mass Styrene		C: Mass LMA		D: Mass DETA (Organic)		E: Mass Water		F: Stirrer Speed		G: Initial Temperature		H: Acid Value		J: Viscosity		2-factor interaction	Error
	A	A^2	B	B^2	C	C^2	D	D^2	E	E^2	F	F^2	G	G^2	H	H^2	J	J^2		
ln(SDevV)	8.07%		1.98%		7.83%		0.01%		9.23%		8.51%		0.01%		7.54%		21.49%		AB: 0.82% AC: 0.91% AD: 0.96% AF: 0.66% AH: 6.83% AJ: 0.77% BD: 1.21% BG: 0.77% BH: 1.91% BJ: 1.43% CH: 0.81% DG: 0.82% DH: 0.80% DJ: 1.34% GH: 0.86% HJ: 3.15%	11.28%
SDevS /µm	3.22%		7.18%		6.83%		0.18%		9.61%		13.98%		0.01%		2.64%		22.46%		AB: 1.34% AC: 0.60% AE: 0.66% AG: 1.05% AH: 3.47% BD: 0.92% BG: 2.89% BH: 1.94% CH: 1.60% DG: 0.73% DJ: 0.54% EG: 0.58% EJ: 0.68% FJ: 1.51% GH: 0.49% HJ: 8.37%	6.48%
CV (VMD)	13.80%		8.43%												11.14%					66.63%
CV (SMD)	0.06%		6.20%		3.70%		3.51%		2.00%		0.14%		0.27%		39.41%		1.55%		AD: 4.11% AH: 10.96% BJ: 4.295 CF: 0.42% CG: 1.04% DH: 10.10% DJ: 0.76%	11.48%
pH					3.38%								8.18%		9.89%					78.54%

Table E.4 – Regressed Equation Coefficients for All Responses (Coded)

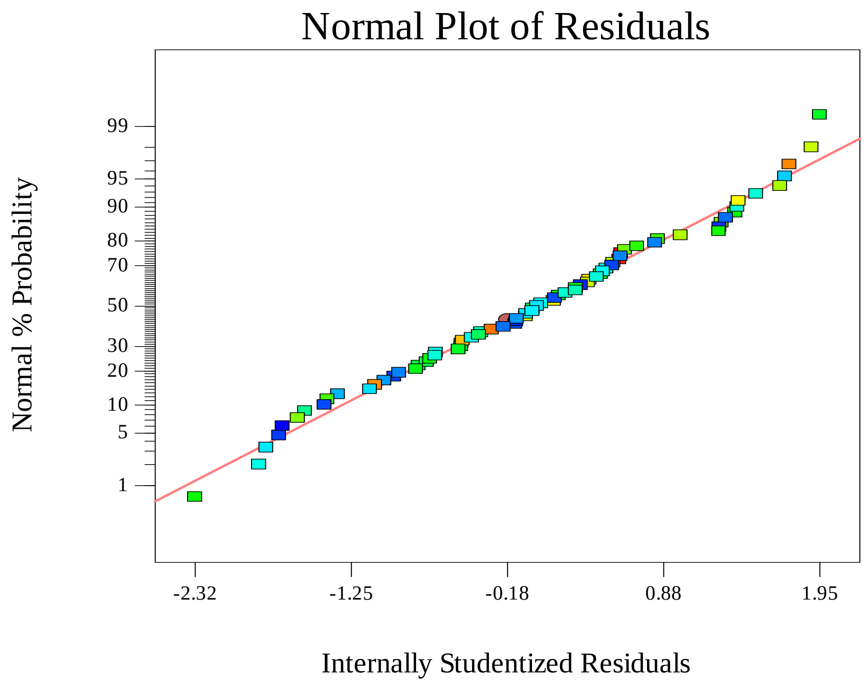
or	Intercept	A: Mass UPR		B: Mass Styrene		C: Mass LMA		D: Mass DETA (Organic)		E: Mass Water		F: Stirrer Speed		G: Initial Reactor Temperature		H: Acid Value		J: Viscosity		2-factor interaction		
onse		A	A^2	B	B^2	C	C^2	D	D^2	E	E^2	F	F^2	G	G^2	H	H^2	J	J^2			
/μm	41.68	-2.61		-4.57		4.74		-0.05		5.39		-7.21		-0.04		3.50		8.03		AB: -2.15 AC: 1.73 AD: -0.55 AE: -1.09 AG: -1.71 AH: 3.70	BD: 1.79 BG: -3.30 BH: -2.17 CH: -1.59 DG: 1.24 DH: -1.37	D EG E FJ GH
o+0.05)	-1.07	-0.098		1.008		0.292		0.386		-0.357		0.095		-0.327		0.017		-0.422		AE: 0.352 BE: -0.319 BG: 0.522 BH: 0.365 CD: 0.450	CH: -0.430 DE: 0.305 DH: 0.477 EG: -0.456 EH: -0.322	EJ FJ: GH GJ H
dm^{-3}	1.0455	3.93E-03				-1.05E-03		-5.76E-05		-2.38E-03		-1.48E-03		3.67E-04		-5.49E-04		-3.00E-04		AG: -1.46E-03 AJ: -1.08E-03 CD: -1.38E-03	CE: -1.07E-03 CF: -1.50E-03 DF: -1.52E-03	EF: EH: GH:
/C	25.051	1.463		0.578				0.180		-0.894		-0.118		0.094		-0.399		-0.086				
cosity)	3.32E-02	4.26E-03		-3.79E-03		-3.39E-03	3.75E-03	-3.75E-03		2.61E-03		-2.53E-04		2.08E-04	-5.57E-03	1.33E-03		1.73E-03		AB: 1.28E-03 AC: 1.46E-03 AD: 1.41E-03 AH: -3.31E-03 AJ: 1.93E-03	BC: -1.35E-03 BH: -1.92E-03 CE: 1.28E-03 DE: -1.35E-03 DH: 3.61E-03	EF: FH: FJ: GH: HJ:
	69.26	-0.90		0.51		0.27		5.00		-2.07		3.96		-2.95		-13.81		-0.40		AB: 1.61 AG: 2.27 AH: -2.10 BG: 1.93	CG: -1.17 DG: -1.16 DH: 2.93 DJ: 0.97	EJ F G H
/kg	5.361	0.273		0.050		0.109		0.014		-0.165												
/μm	18.31	-0.92		-3.18		1.40		0.70		1.69		-3.13		-0.03		-1.38		2.87		AB: -1.13 AC: 0.74 AD: 0.63 AE: -0.97 BG: -1.49	BJ: -0.76 CH: -1.36 DG: 0.80 DH: 0.86	E F FJ H
evV)	3.030	-0.133		-0.069		0.137		-0.005		0.149		-0.148		0.003		0.127		0.211		AB: -0.048 AC: 0.051 AD: -0.049 AF: -0.042 AH: 0.127 AJ: 0.041	BD: 0.054 BG: -0.044 BH: -0.066 BJ: 0.060 CH: -0.043	DG DH DJ GH HJ

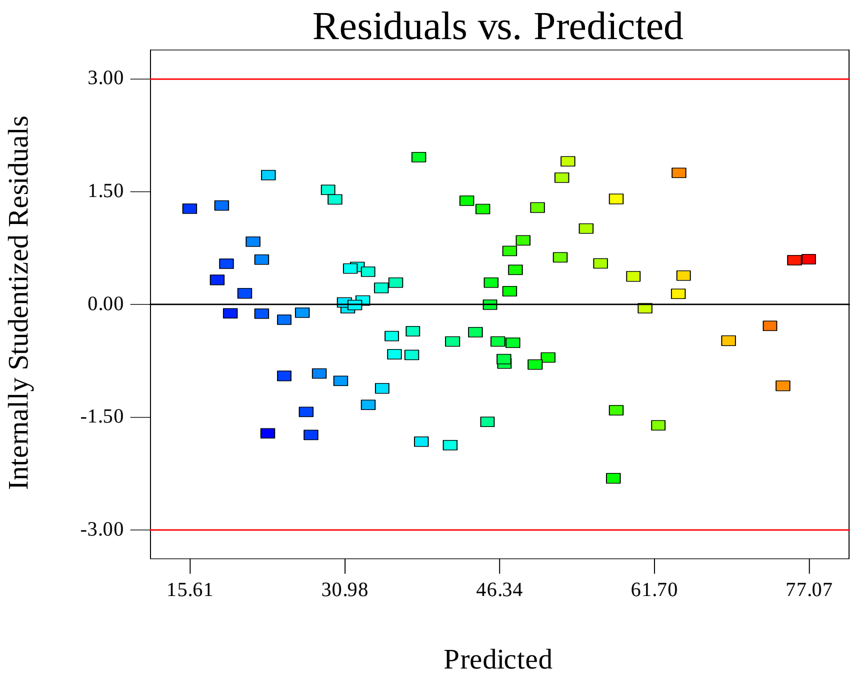
or	Intercept	A: Mass UPR		B: Mass Styrene		C: Mass LMA		D: Mass DETA (Organic)		E: Mass Water		F: Stirrer Speed		G: Initial Reactor Temperature		H: Acid Value		J: Viscosity		2-factor interaction		
onse		A	A^2	B	B^2	C	C^2	D	D^2	E	E^2	F	F^2	G	G^2	H	H^2	J	J^2			
/μm	20.14	-1.48		-2.34		2.24		0.35		2.62		-3.53		-0.09		1.32		3.82		AB: -1.06 AC: 0.73 AE: -0.71 AG: -0.90 AH: 1.59 BD: 0.83	BG: -1.48 BH: -1.17 CH: -1.06 DG: 0.76 DJ: 0.63	EG E FJ GH H
MD)	54.24	-2.73		2.17												2.39						
MD)	112.66	-0.71		7.46		5.80		-5.56		4.35		-1.14		1.56		17.82		3.53		AD: -6.30 AH: 10.06 BJ: 6.39	CF: 2.08 CG: 3.21	DH D
	8.17					-0.06								0.09		-0.09						

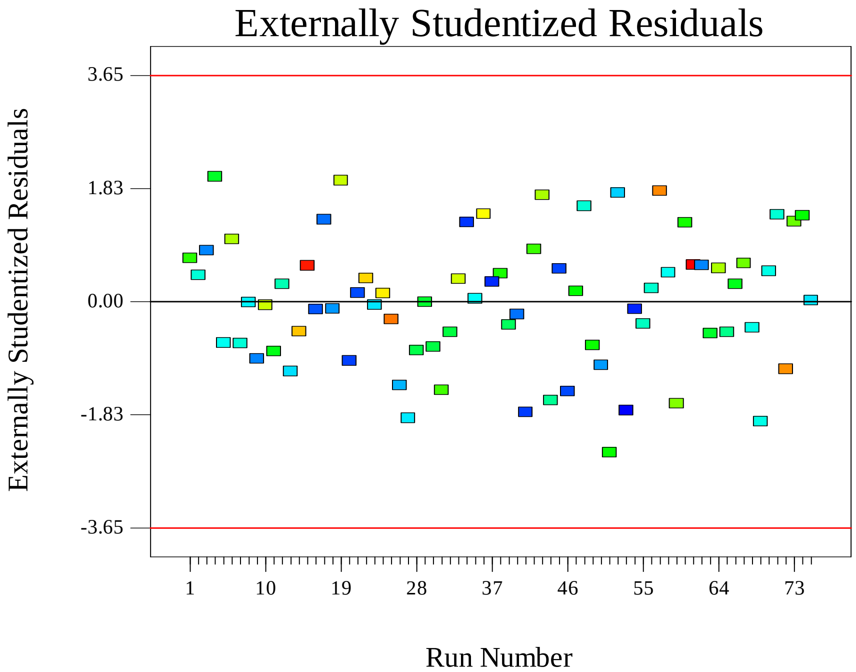
Table E.5: Model Summary Statistics for the VMD Response

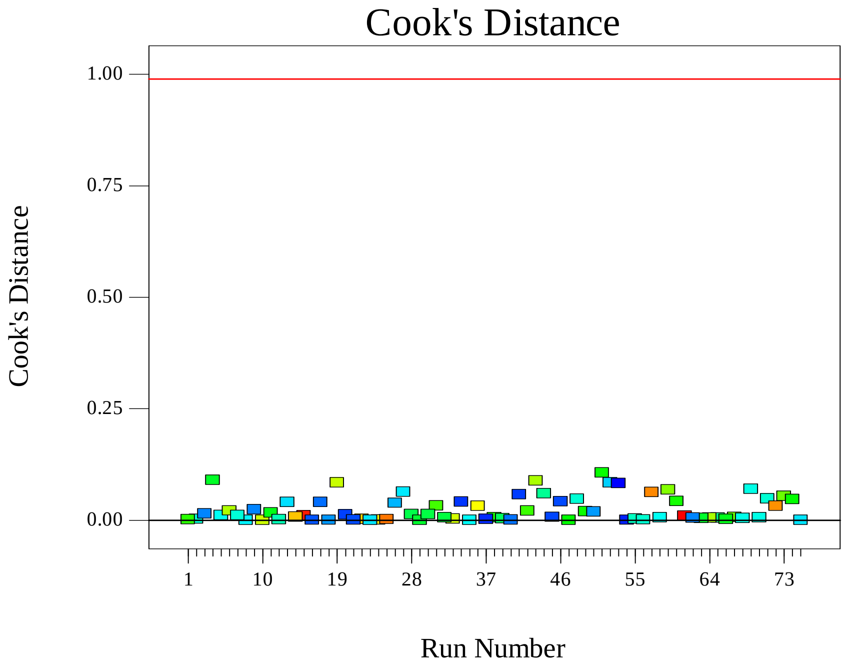
Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	9.80	0.67	0.62	0.56	
2FI	**5.12**	**0.96**	**0.90**	**0.63**	**Suggested**
Quadratic	5.40	0.97	0.89	0.45	Aliased
Cubic	4.41	1.00	0.92	-	Aliased

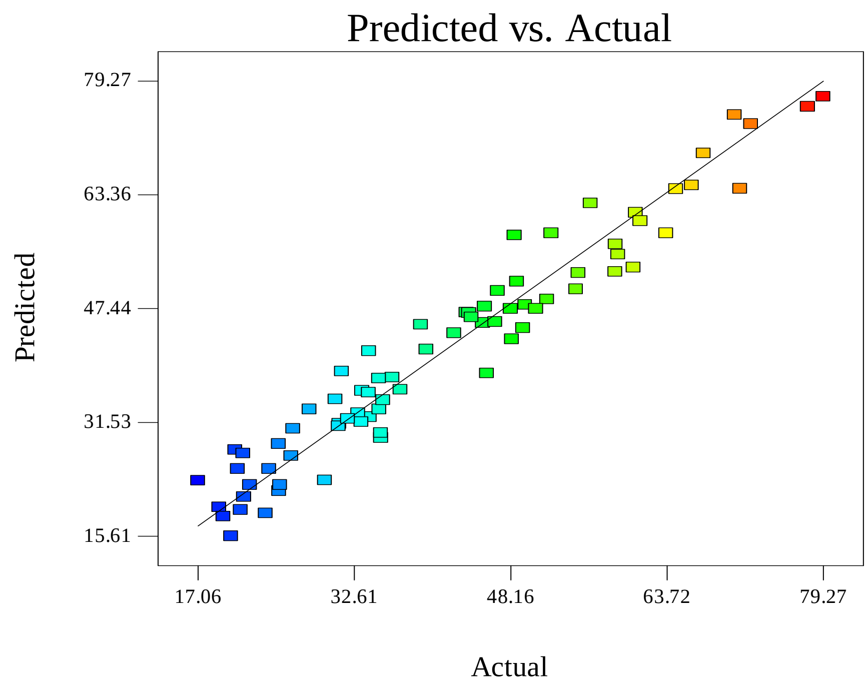
Figure E.1: Diagnostic Charts for the VMD (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
3.65
1.83
0.00
-1.83
-3.65
Externally Studentized Residuals
1
10
19
28
37
46
55
64
73
Run Number


Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
10
19
28
37
46
55
64
73
Run Number

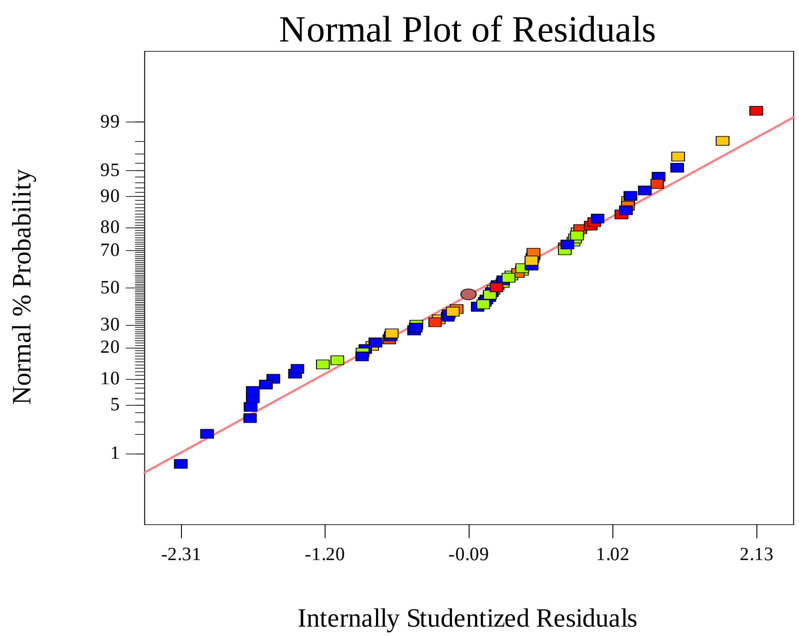


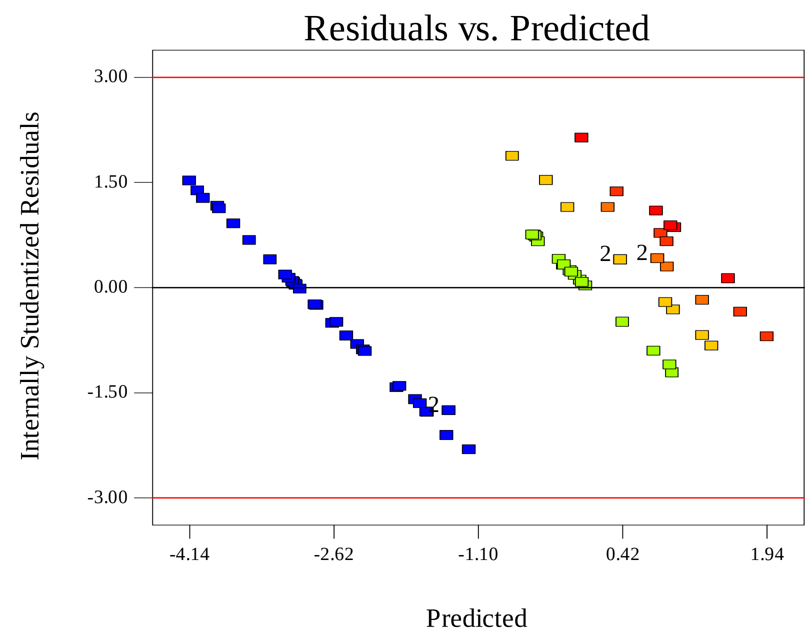
Predicted vs. Actual
79.27
63.36
47.44
31.53
15.61
Predicted
17.06
32.61
48.16
63.72
79.27
Actual

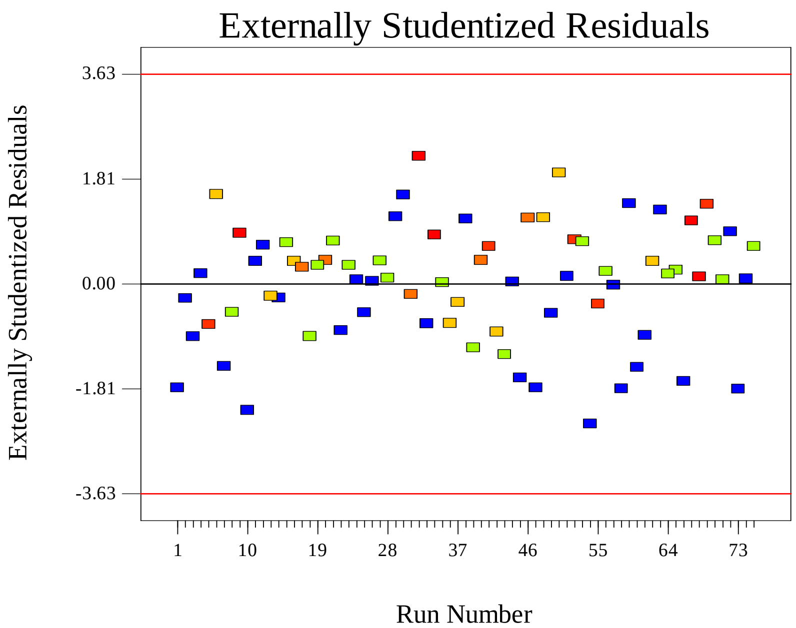
Table E.6: Model Summary Statistics for the ln(Buildup+0.05) Response

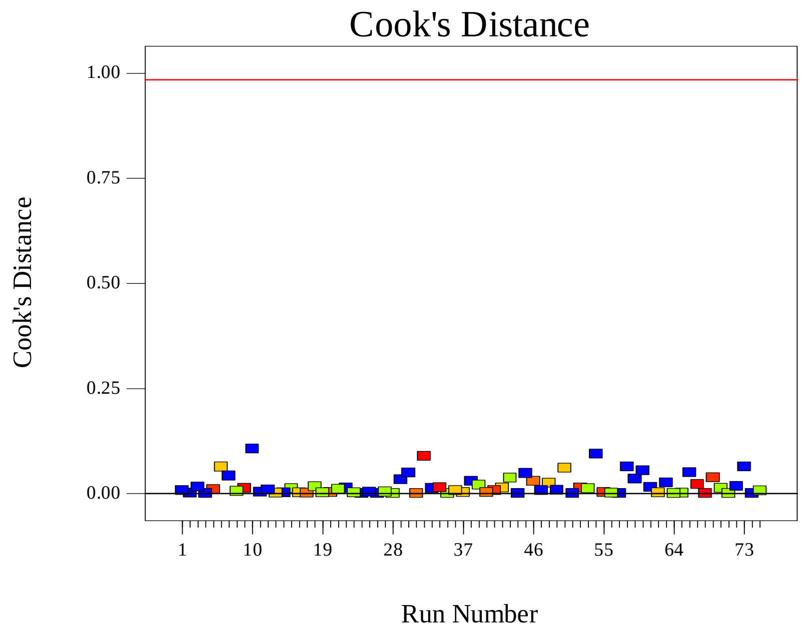
Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	1.47	0.46	0.39	0.28	
2FI	**1.05**	**0.88**	**0.69**	**0.20**	**Suggested**
Quadratic	1.02	0.91	0.71	-0.32	Aliased
Cubic	0.14	1.00	0.99	-	Aliased

Figure E.2: Diagnostic Charts for the ln(Buildp+0.05) (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
Externally Studentized Residuals
3.63
1.81
0.00
-1.81
-3.63
1
10
19
28
37
46
55
64
73
Run Number


Cook's Distance
Cook's Distance
1.00
0.75
0.50
0.25
0.00
1
10
19
28
37
46
55
64
73
Run Number

5

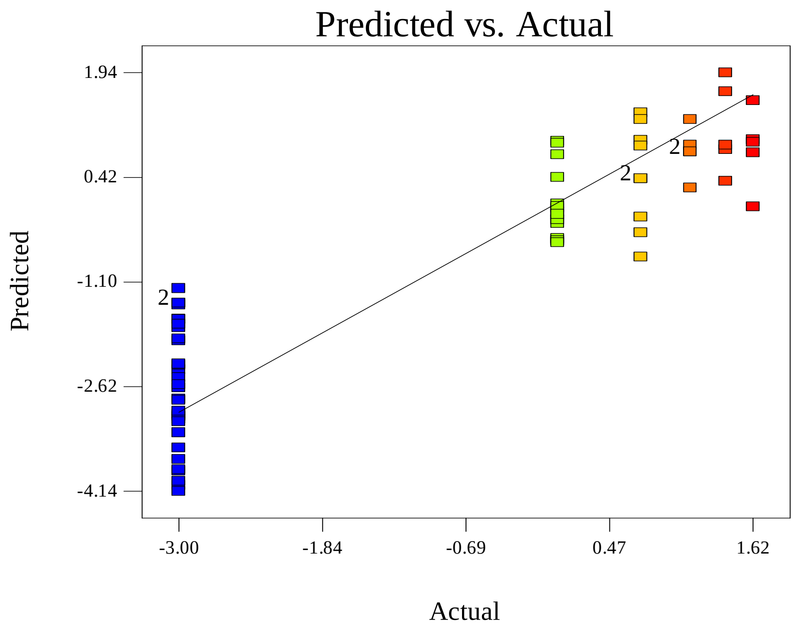
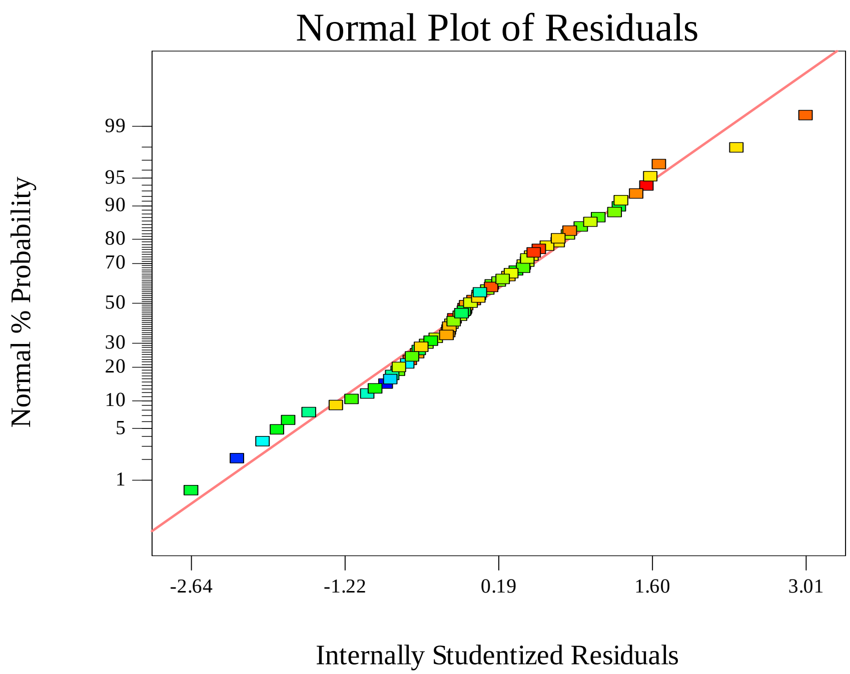
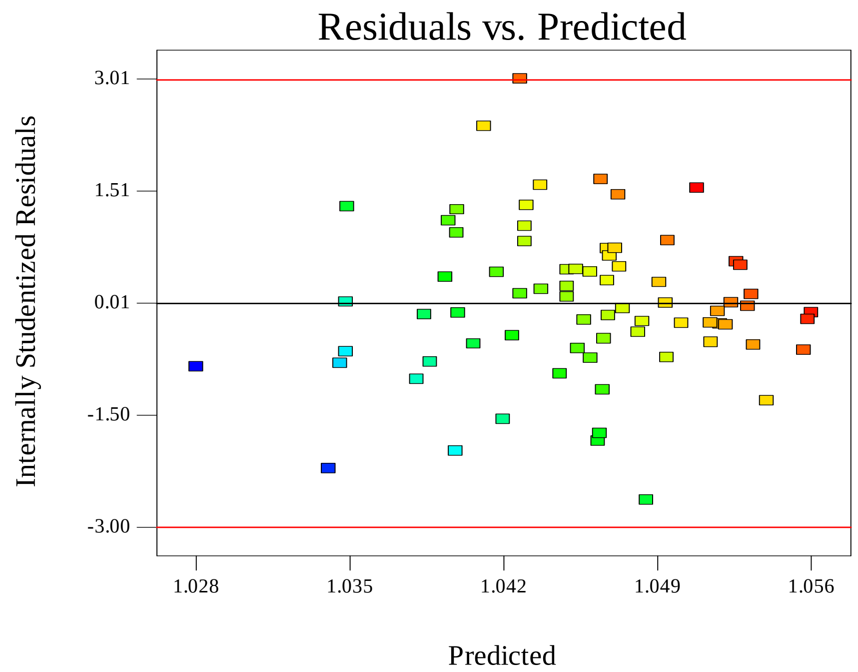

Predicted vs. Actual
1.94
0.42
-1.10
-2.62
-4.14
Predicted
2
2
2
-3.00
-1.84
-0.69
0.47
1.62
Actual

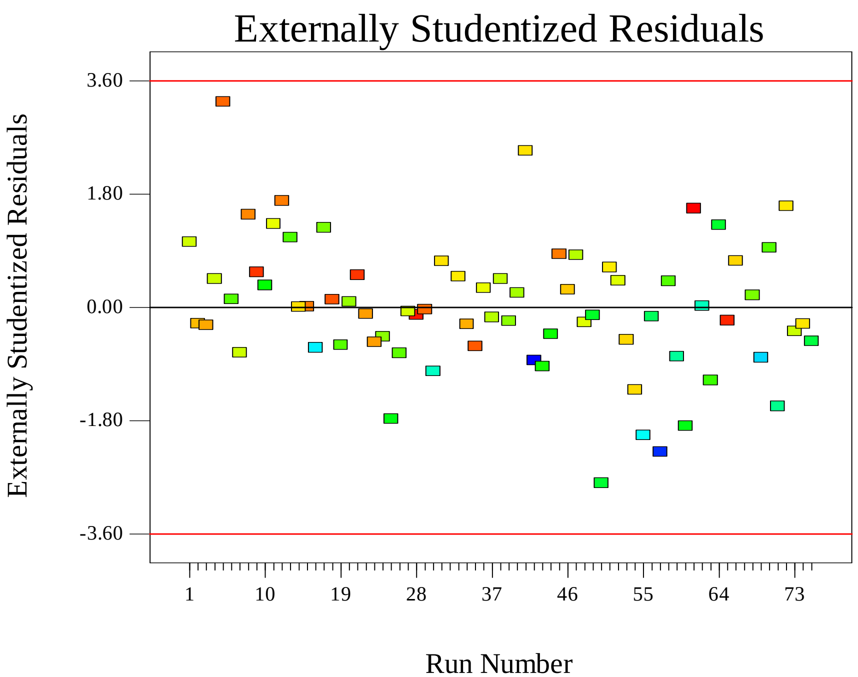
Table E.7: Model Summary Statistics for the SG Response

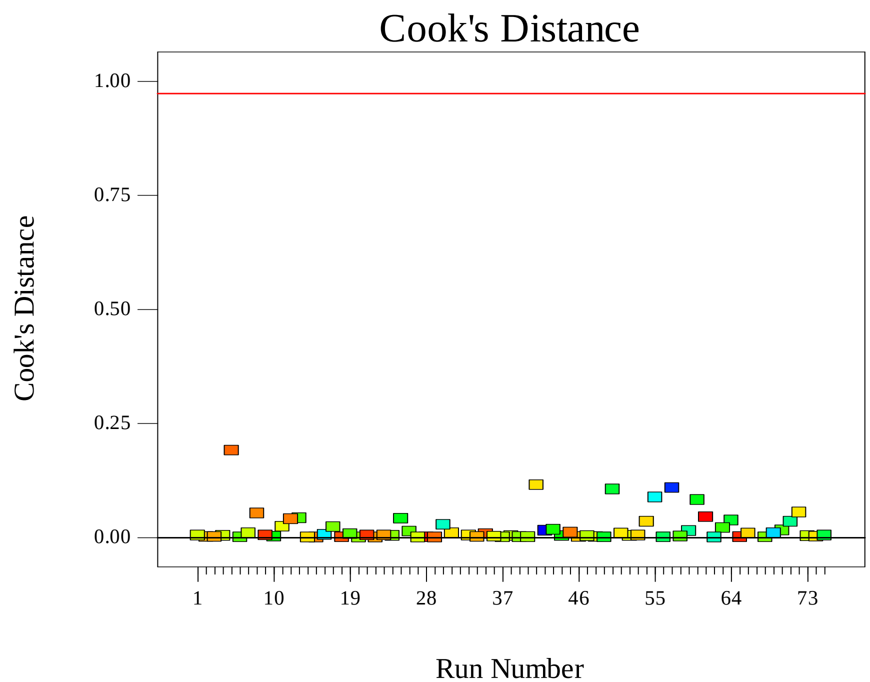
Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	**0.01**	**0.49**	**0.42**	**0.32**	**Suggested**
2FI	0.00	0.81	0.50	-0.71	
Quadratic	0.00	0.86	0.51	-1.43	Aliased
Cubic	0.00	1.00	0.98		Aliased

Figure E.3: Diagnostic Charts for the SG (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
3.60
1.80
0.00
-1.80
-3.60
Externally Studentized Residuals
1
10
19
28
37
46
55
64
73
Run Number


Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
10
19
28
37
46
55
64
73
Run Number

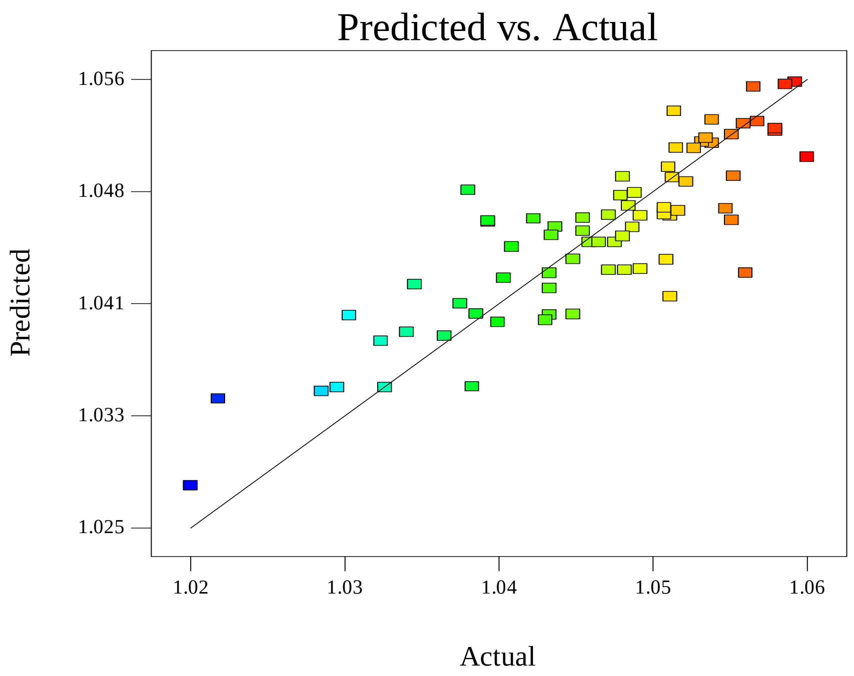
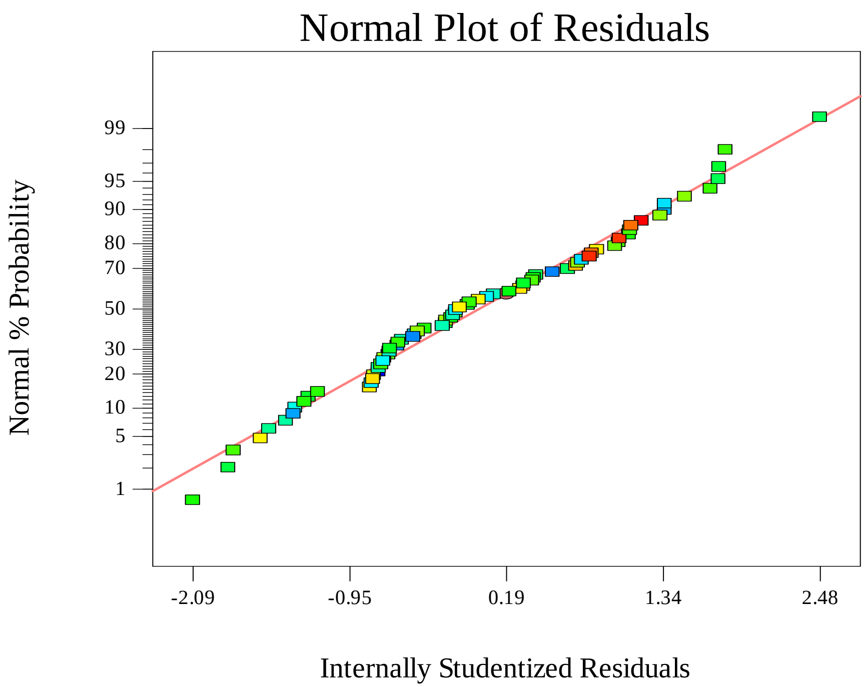
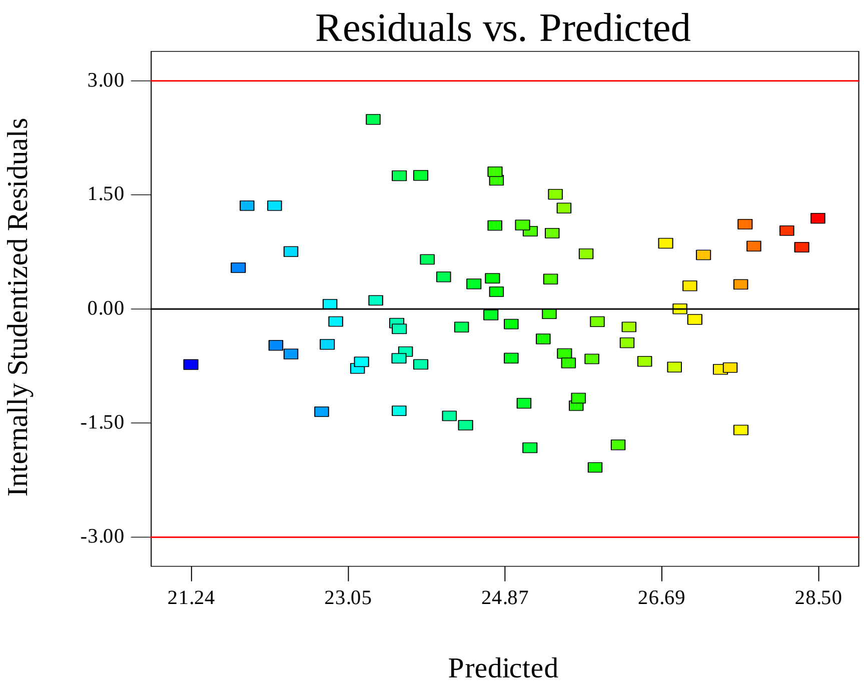

Predicted vs. Actual
1.056
1.048
1.041
1.033
1.025
1.02
1.03
1.04
1.05
1.06
Predicted
Actual

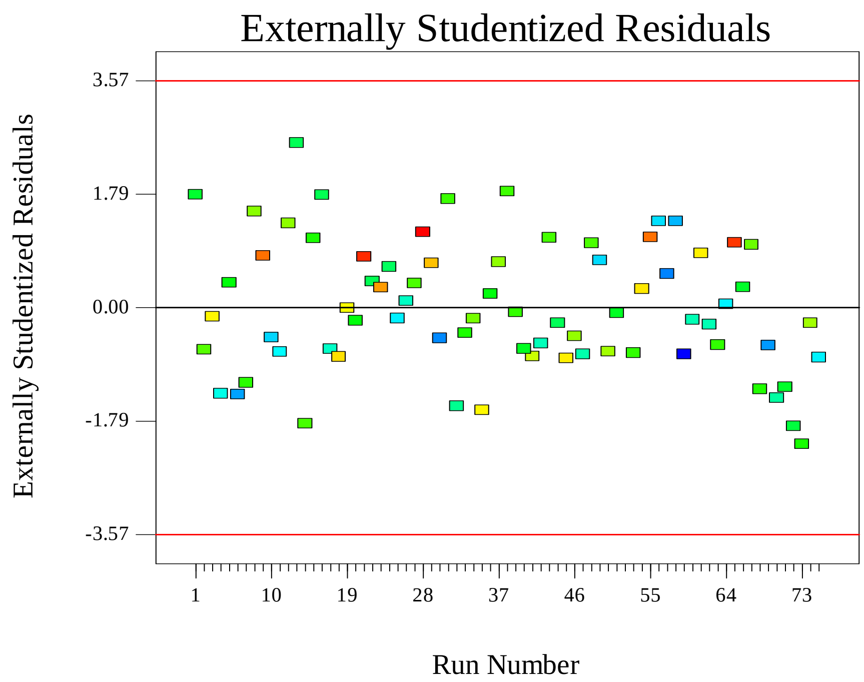
Table E.8: Model Summary Statistics for the %NVC Response

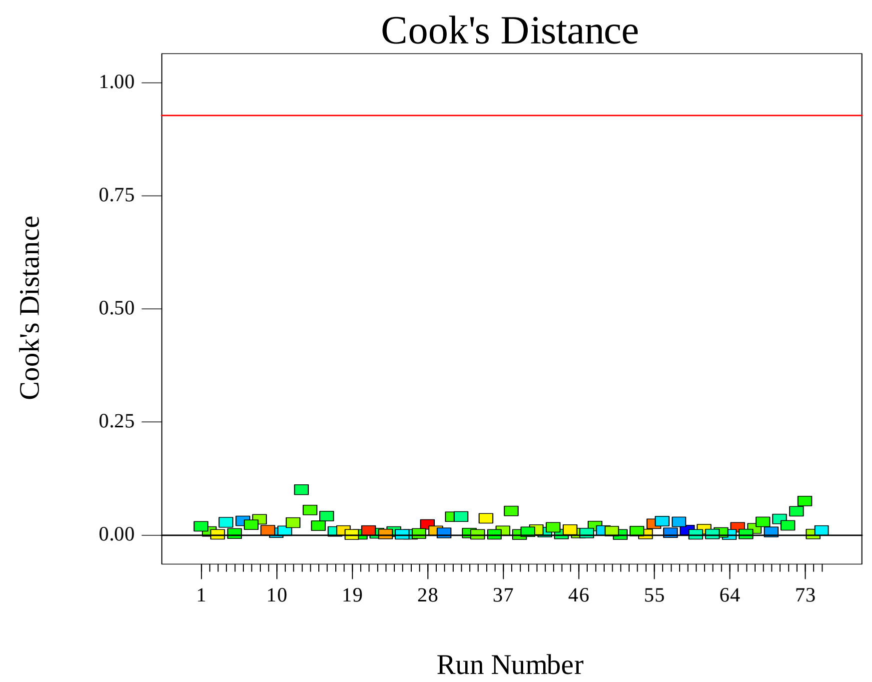
Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	**0.40**	**0.96**	**0.95**	**0.94**	**Suggested**
2FI	0.37	0.98	0.96	0.88	
Quadratic	0.36	0.99	0.96	0.86	Aliased
Cubic	0.49	1.00	0.93		Aliased

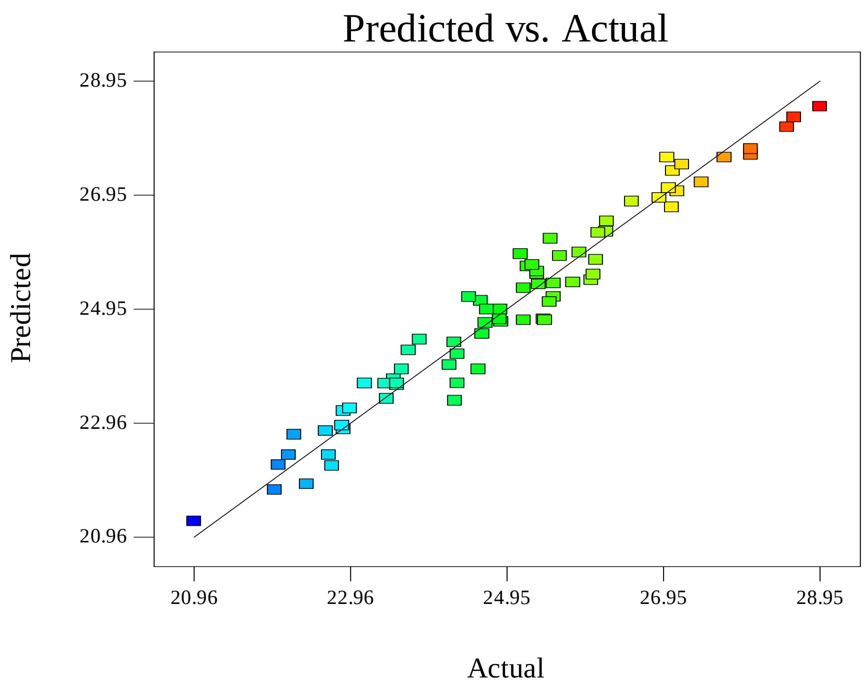
Figure E.4: Diagnostic Charts for the %NVC (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
3.57
1.79
0.00
-1.79
-3.57
Externally Studentized Residuals
1
10
19
28
37
46
55
64
73
Run Number


Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
10
19
28
37
46
55
64
73
Run Number

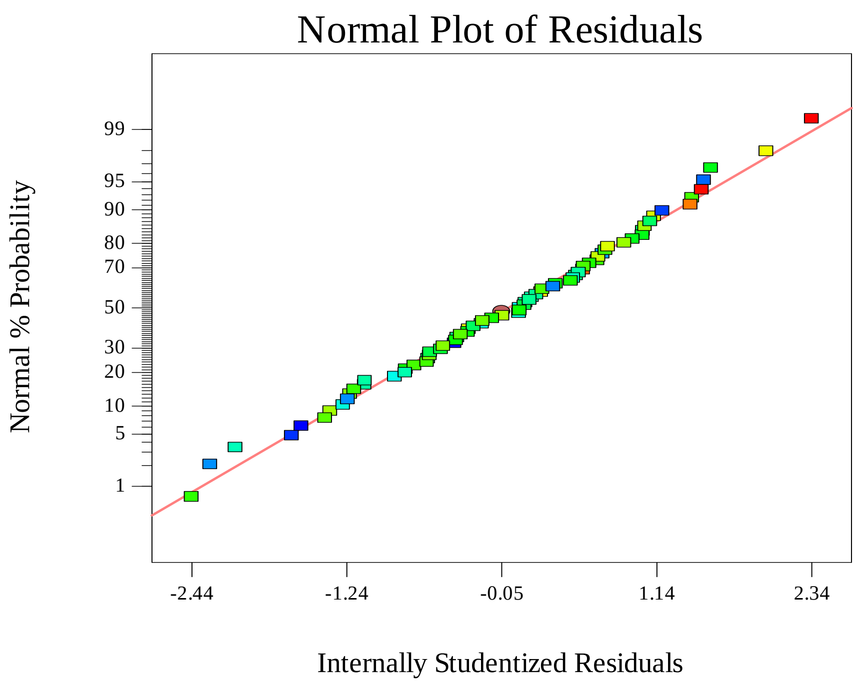


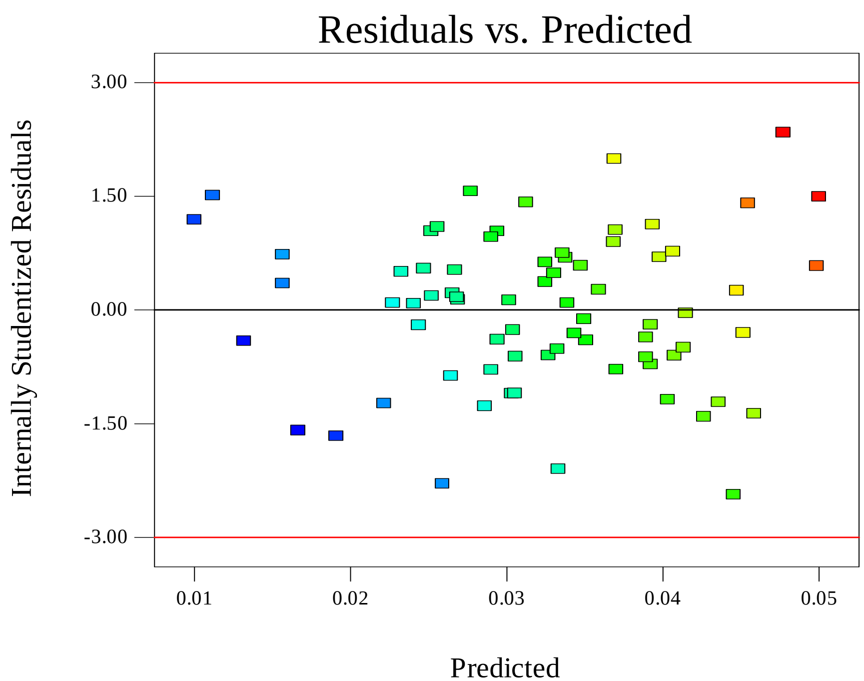
Predicted vs. Actual
28.95
26.95
24.95
22.96
20.96
Predicted
20.96
22.96
24.95
26.95
28.95
Actual

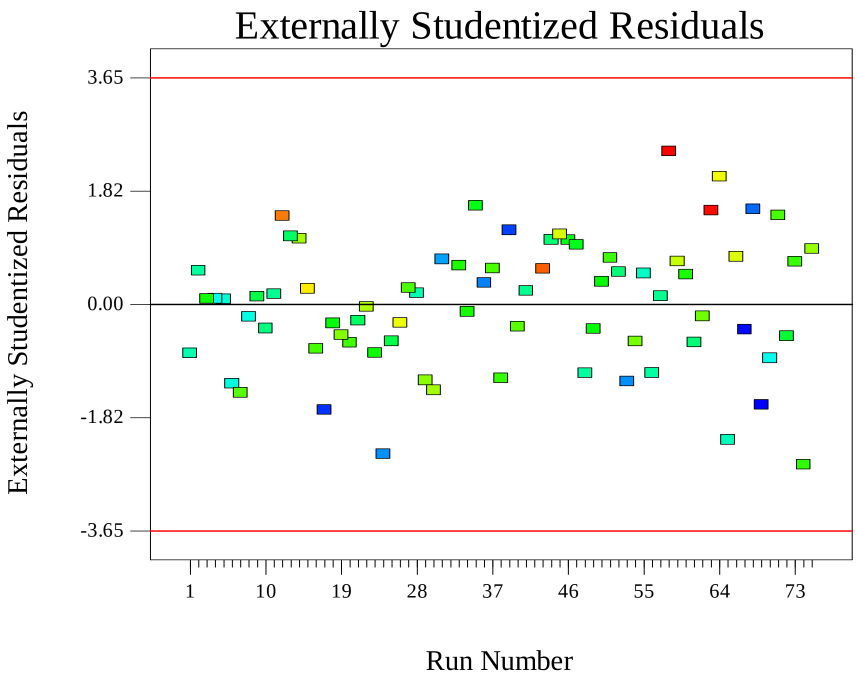
Table E.9: Model Summary Statistics for the $1/\sqrt{Viscosity}$ Response

Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	0.010	0.33	0.23	0.10	
2FI	**0.006**	**0.89**	**0.72**	**0.14**	**Suggested**
Quadratic	0.006	0.93	0.74	-0.05	Aliased
Cubic	0.003	1.00	0.93		Aliased

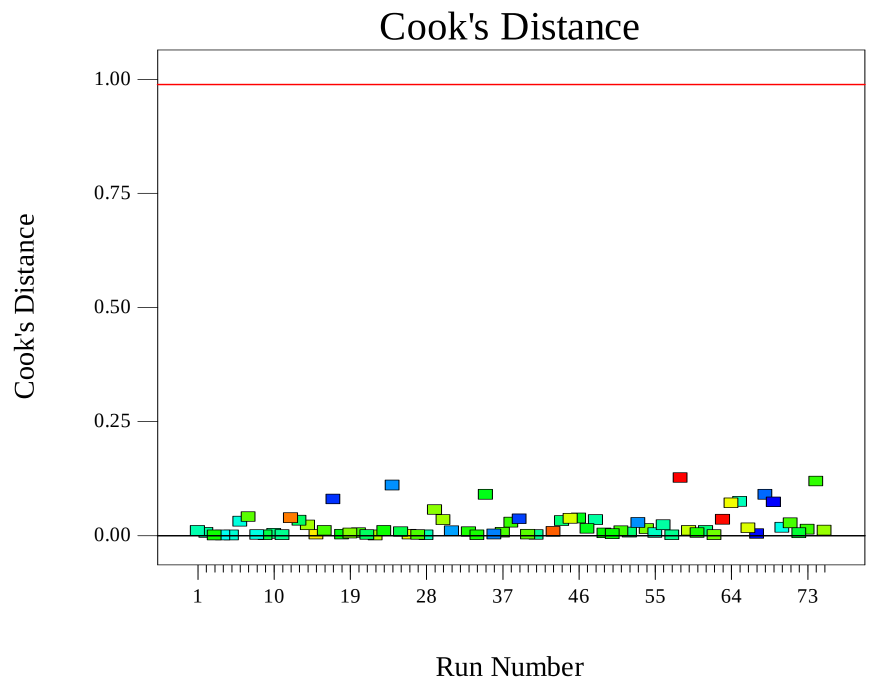
Figure E.5: Diagnostic Charts for the $1/\sqrt{Viscosity}$ (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.







Externally Studentized Residuals
3.65
1.82
0.00
-1.82
-3.65
Externally Studentized Residuals
1
10
19
28
37
46
55
64
73
Run Number



Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
10
19
28
37
46
55
64
73
Run Number

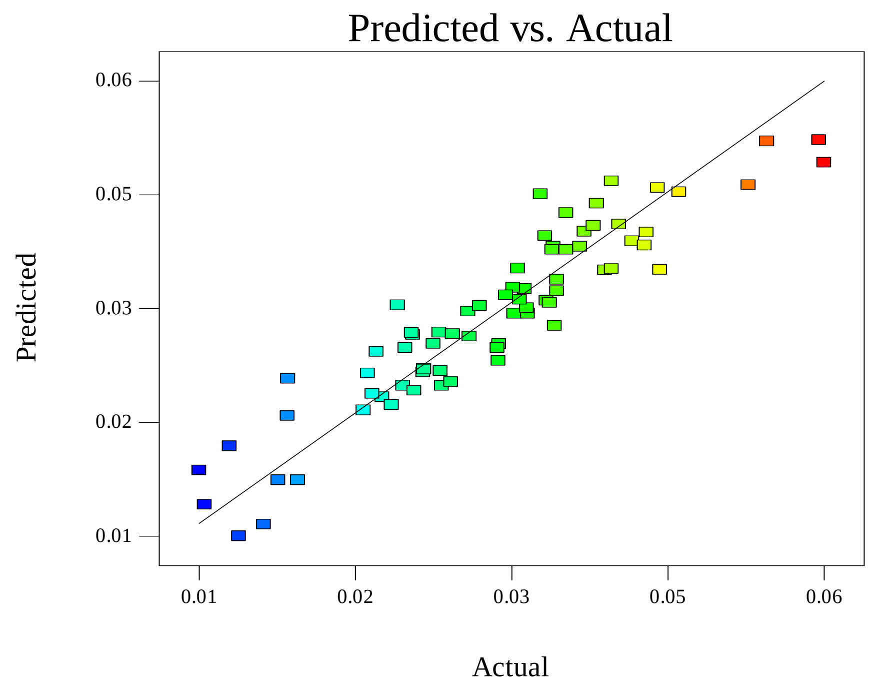
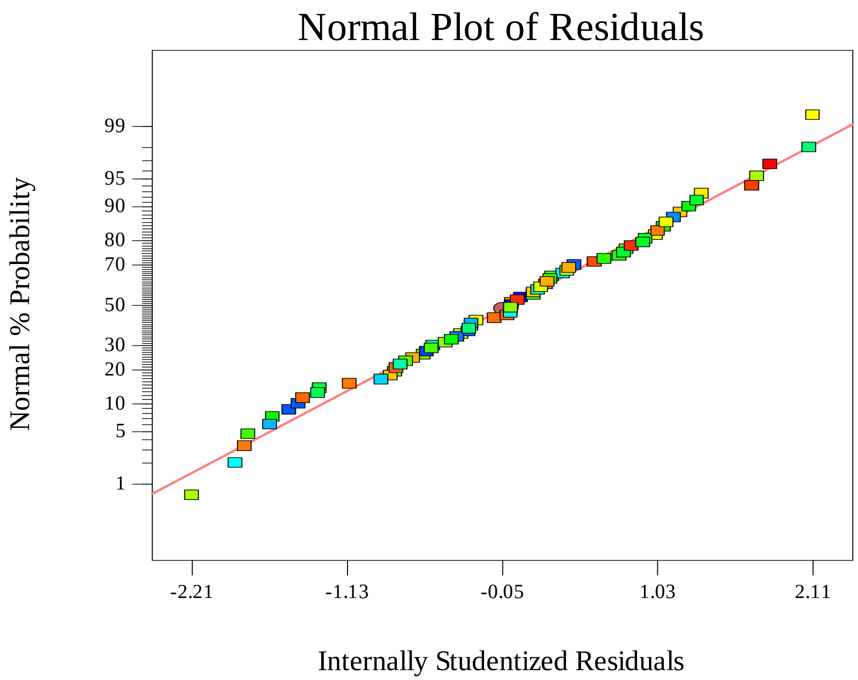
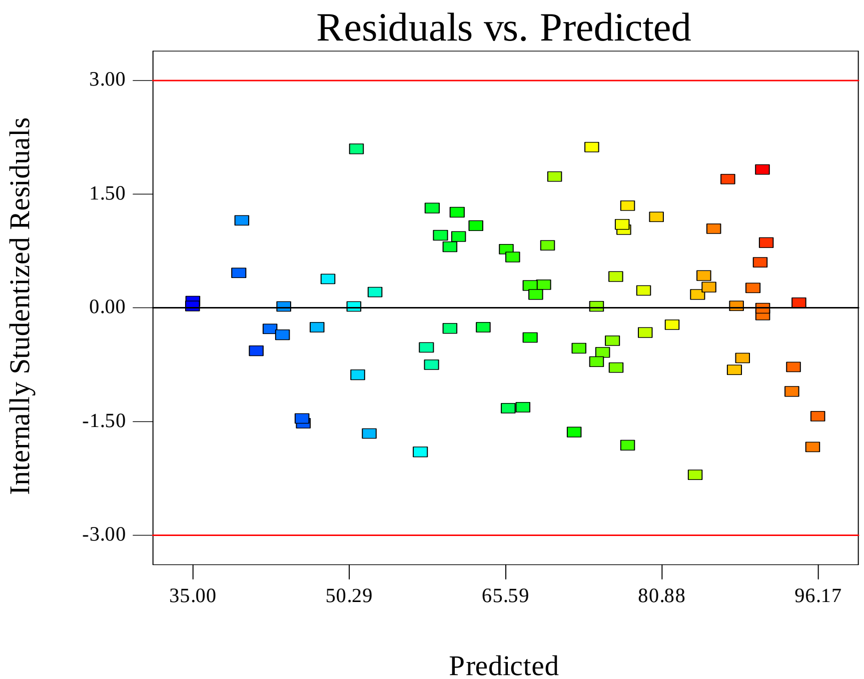

Predicted vs. Actual
0.06
0.05
0.03
0.02
0.01
Predicted
0.01
0.02
0.03
0.05
0.06
Actual

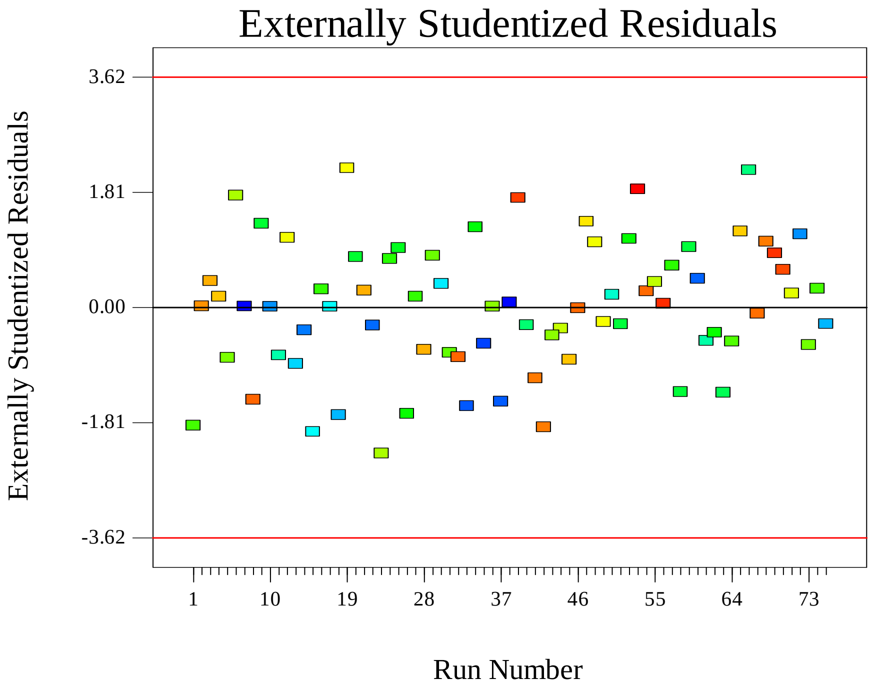
Table E.10: Model Summary Statistics for the Contrast Ratio Response

Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	8.19	0.80	0.78	0.74	
2FI	**4.85**	**0.97**	**0.92**	**0.76**	**Suggested**
Quadratic	5.26	0.97	0.91	0.61	Aliased
Cubic	4.94	1.00	0.92		Aliased

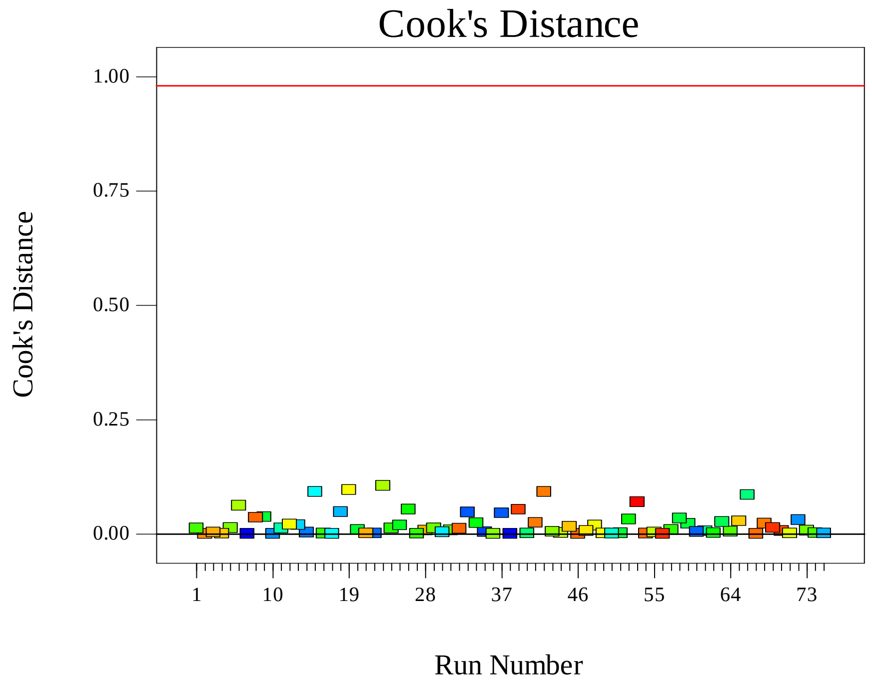
Figure E.6: Diagnostic Charts for the Contrast Ratio (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.







Externally Studentized Residuals
3.62
1.81
0.00
-1.81
-3.62
Externally Studentized Residuals
1
10
19
28
37
46
55
64
73
Run Number



Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
10
19
28
37
46
55
64
73
Run Number

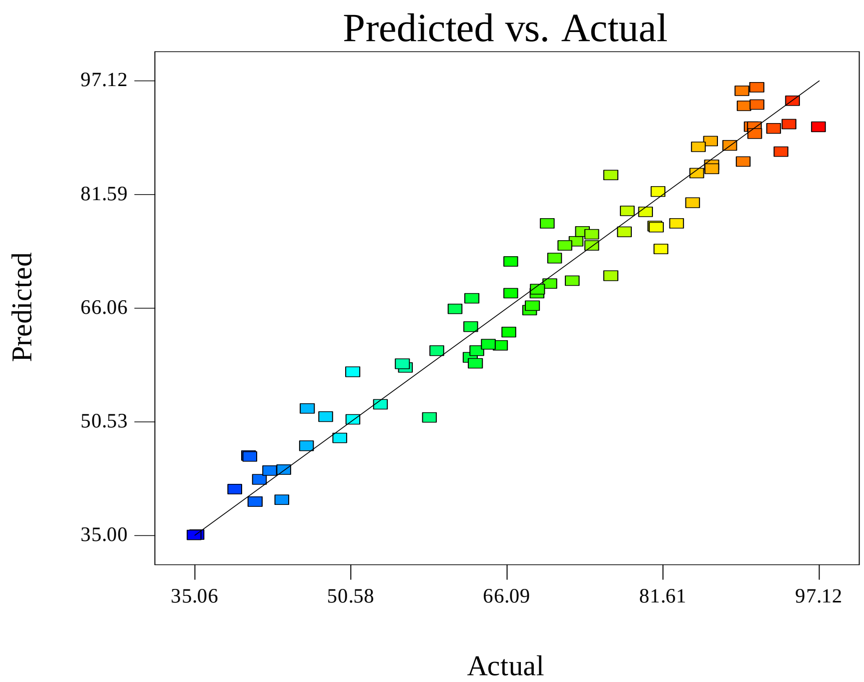
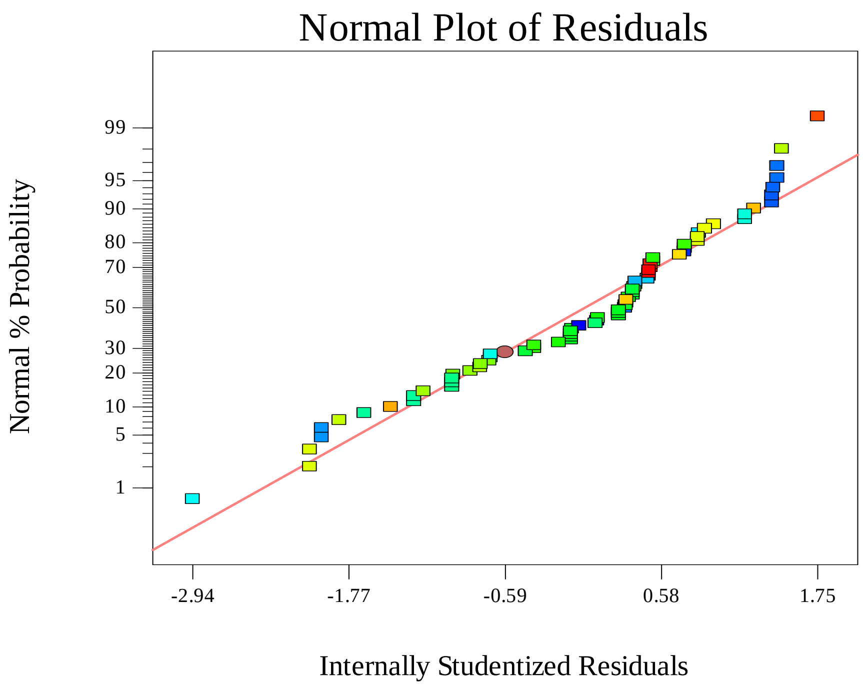
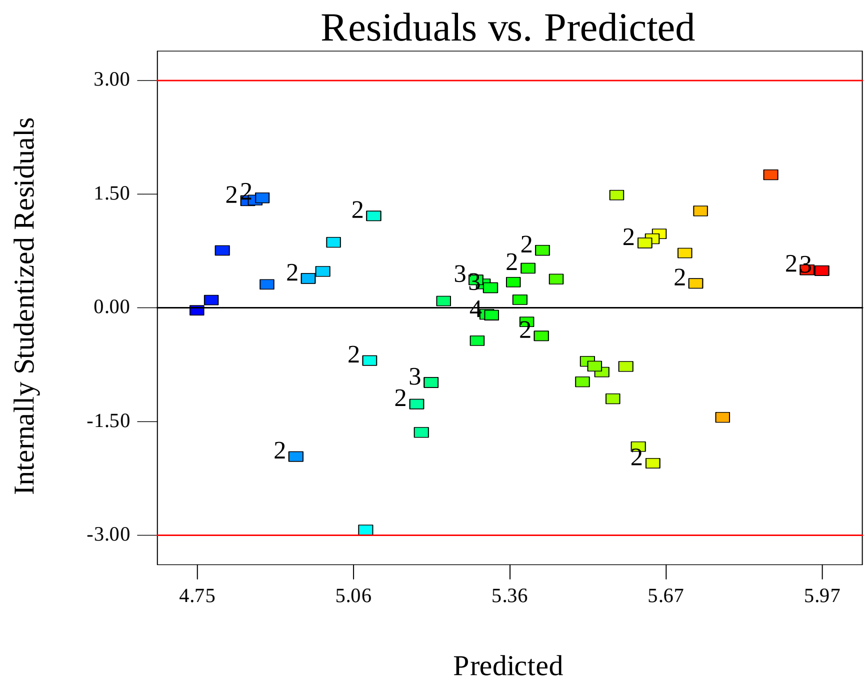

Predicted vs. Actual
97.12
81.59
66.06
50.53
35.00
Predicted
35.06
50.58
66.09
81.61
97.12
Actual

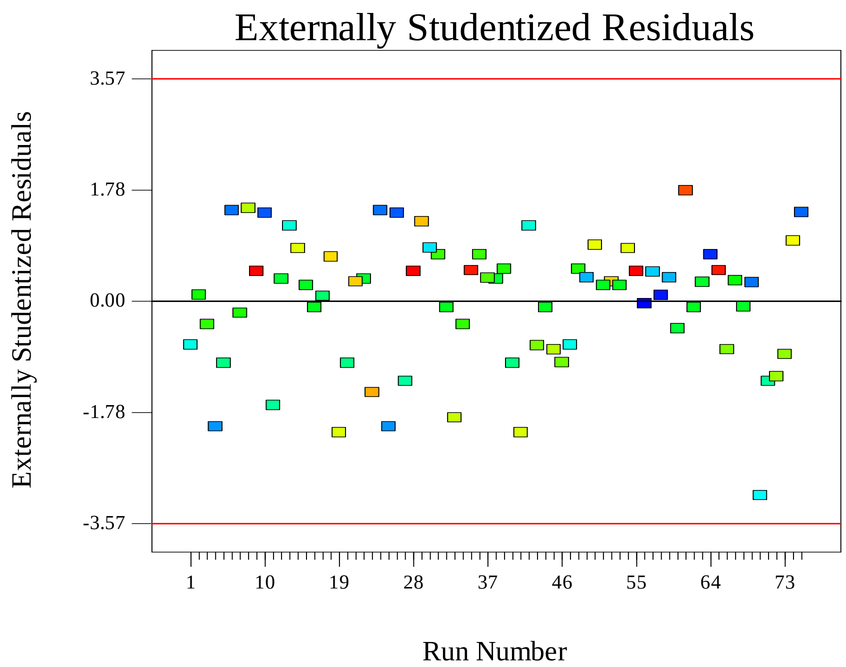
Table E.11: Model Summary Statistics for the Cost/kg Response

Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	**0.01**	**1.00**	**1.00**	**1.00**	
2FI	0.00	1.00	1.00	1.00	Suggested
Quadratic	0.00	1.00	1.00	1.00	Aliased
Cubic	0.00	1.00	1.00		Aliased

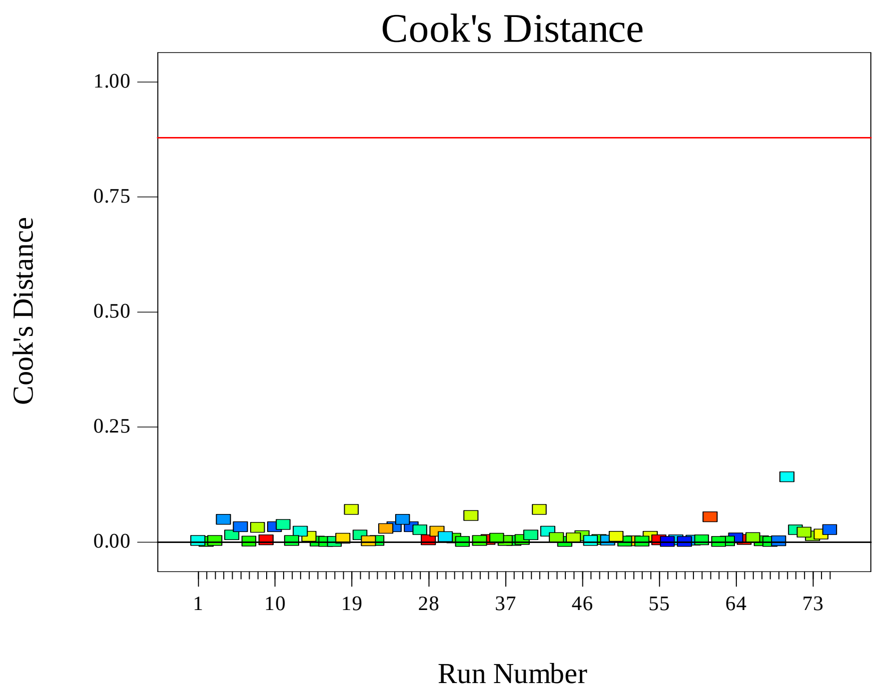
Figure E.7: Diagnostic Charts for the Cost/kg (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.



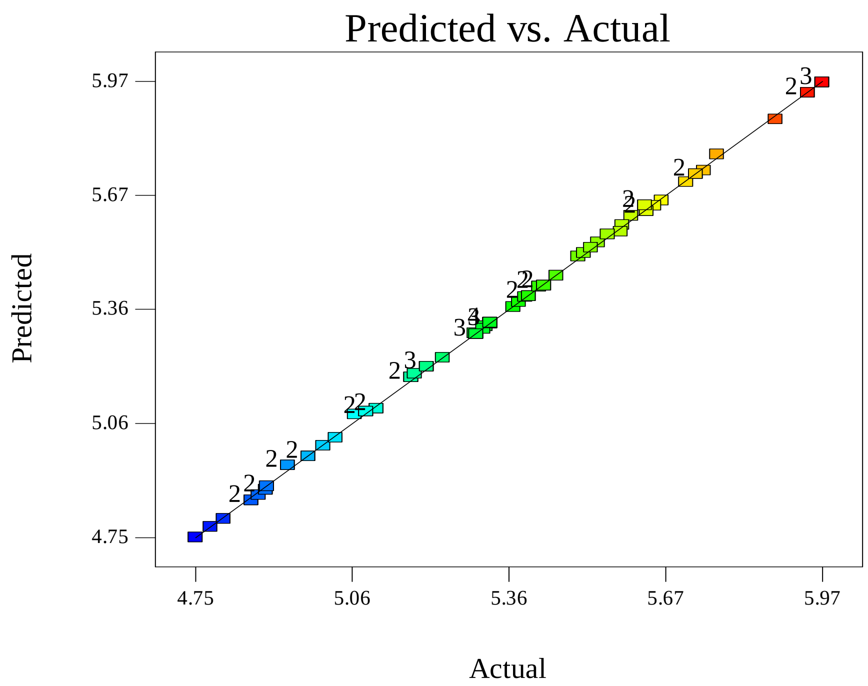




Externally Studentized Residuals
3.57
1.78
0.00
-1.78
-3.57
Externally Studentized Residuals
1
10
19
28
37
46
55
64
73
Run Number



Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
10
19
28
37
46
55
64
73
Run Number

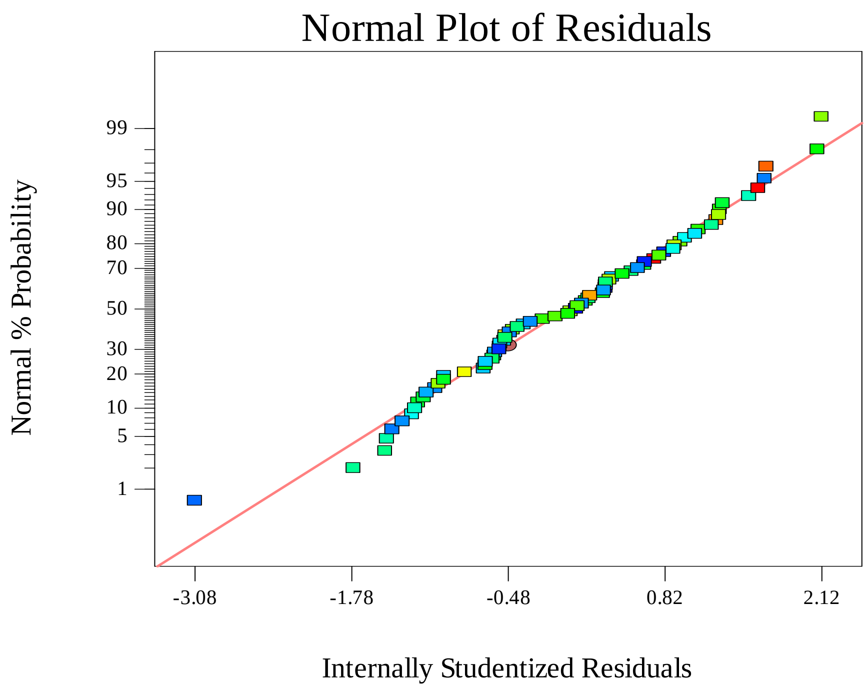


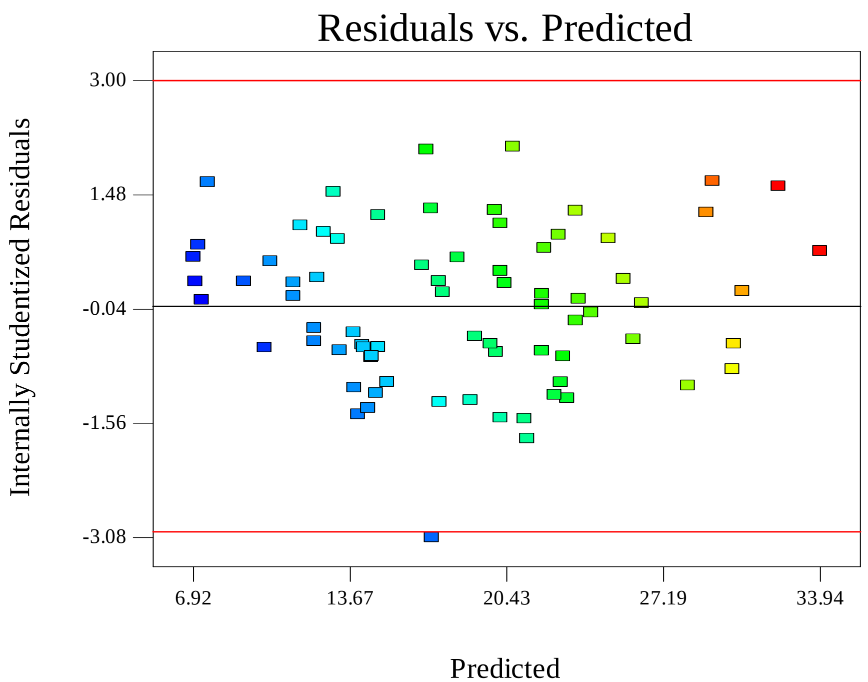
Predicted vs. Actual
Predicted
Actual
5.97
5.67
5.36
5.06
4.75
4.75
5.06
5.36
5.67
5.97

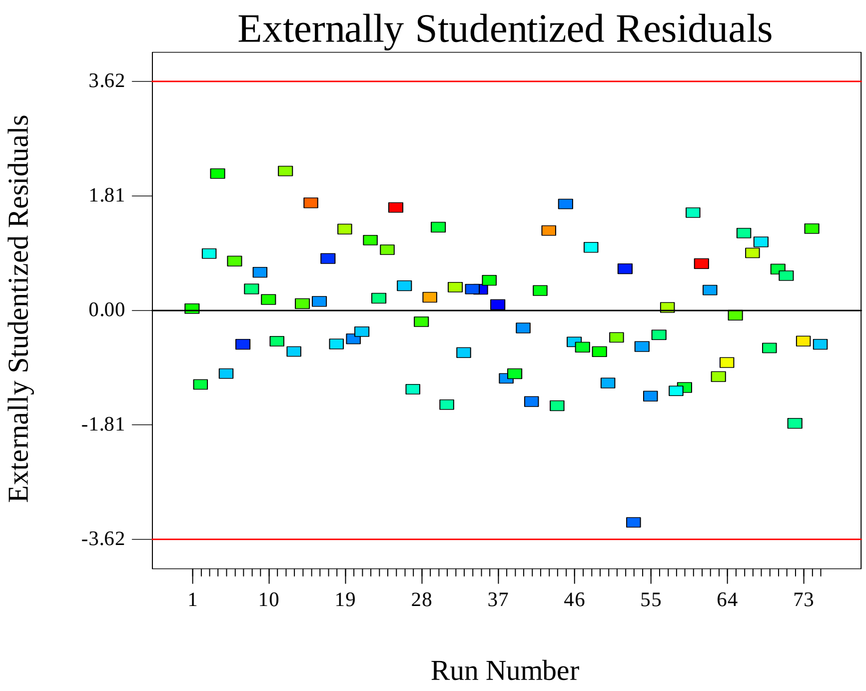
Table E.12: Model Summary Statistics for the SMD Response

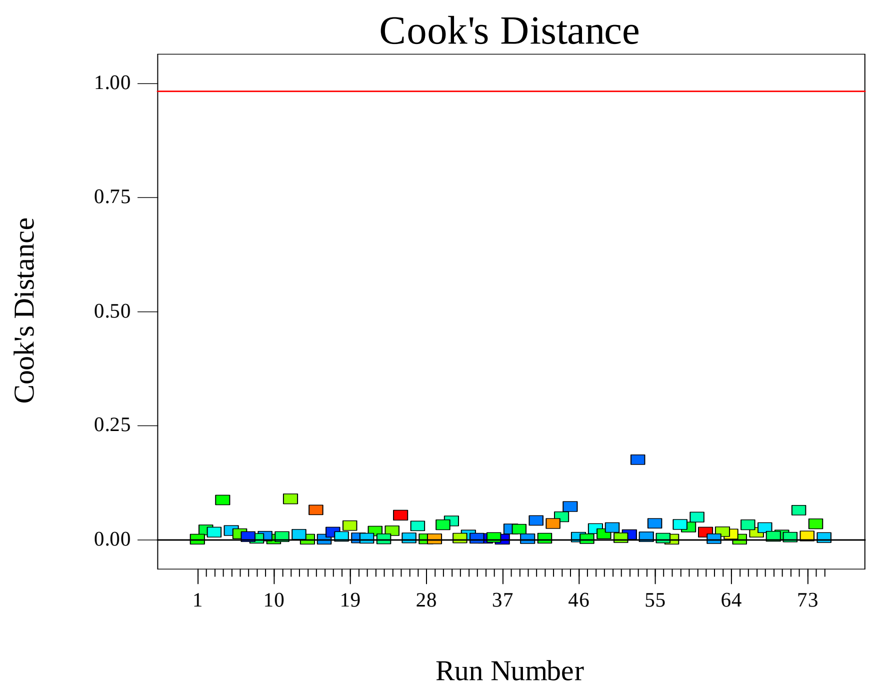
Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	4.28	0.66	0.61	0.55	
2FI	**2.69**	**0.94**	**0.85**	**0.47**	**Suggested**
Quadratic	2.75	0.95	0.84	0.27	Aliased
Cubic	1.65	1.00	0.94		Aliased

Figure E.8: Diagnostic Charts for the SMD (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
3.62
1.81
0.00
-1.81
-3.62
Externally Studentized Residuals
1
10
19
28
37
46
55
64
73
Run Number


Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
10
19
28
37
46
55
64
73
Run Number

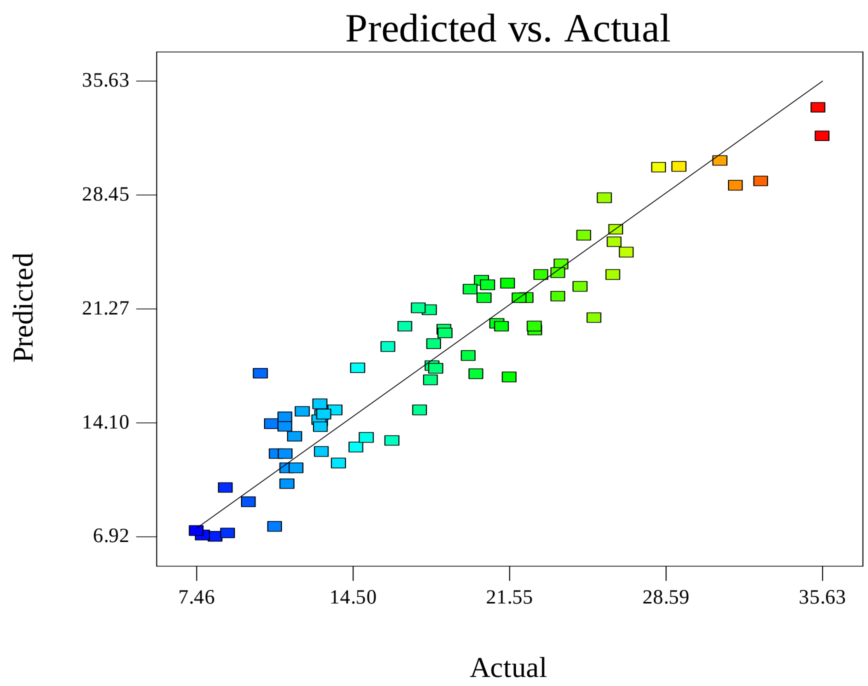
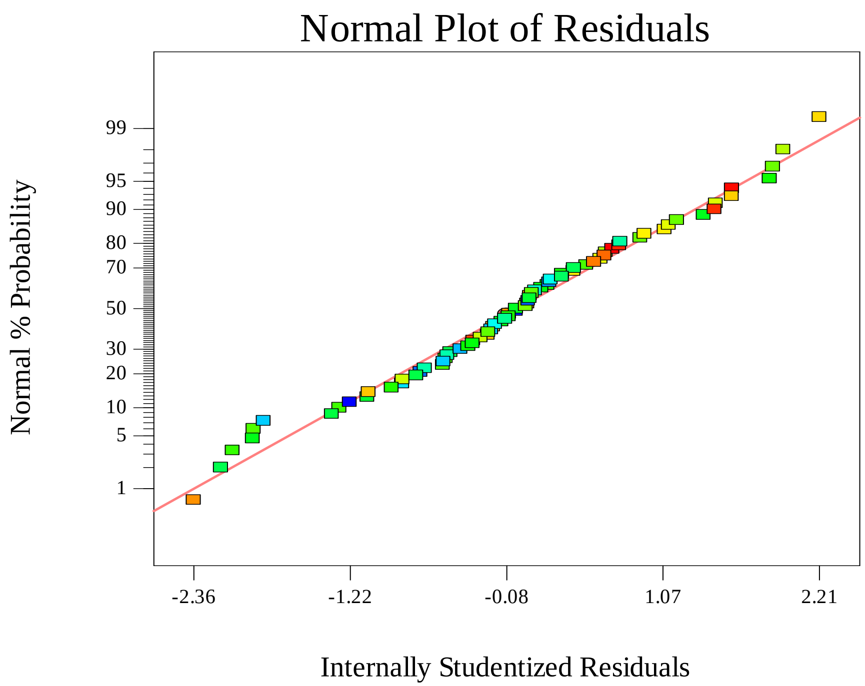
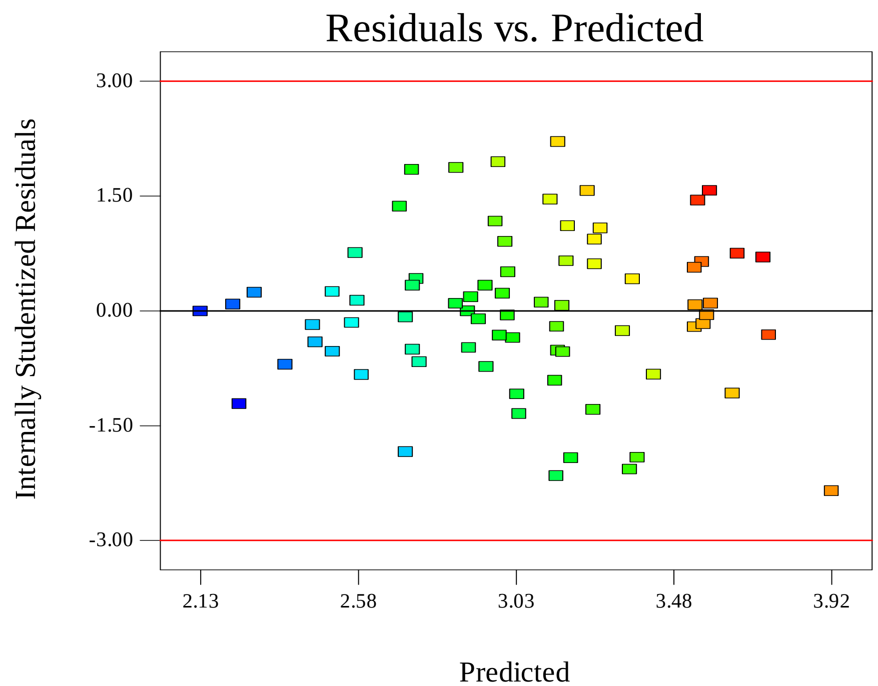

Predicted vs. Actual
35.63
28.45
21.27
14.10
6.92
Predicted
7.46
14.50
21.55
28.59
35.63
Actual

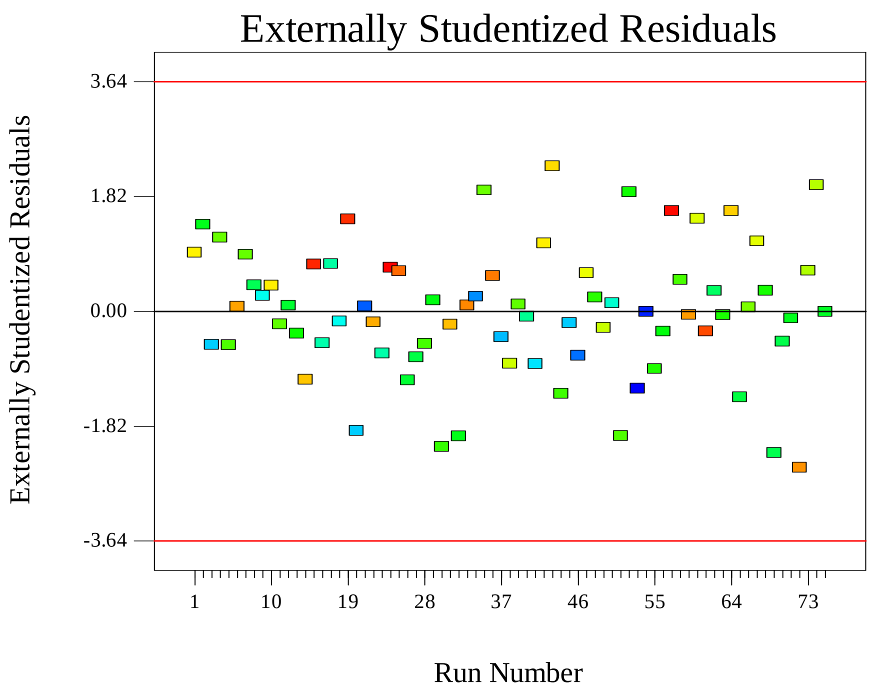
Table E.13: Model Summary Statistics for the $\ln(SDevV)$Response

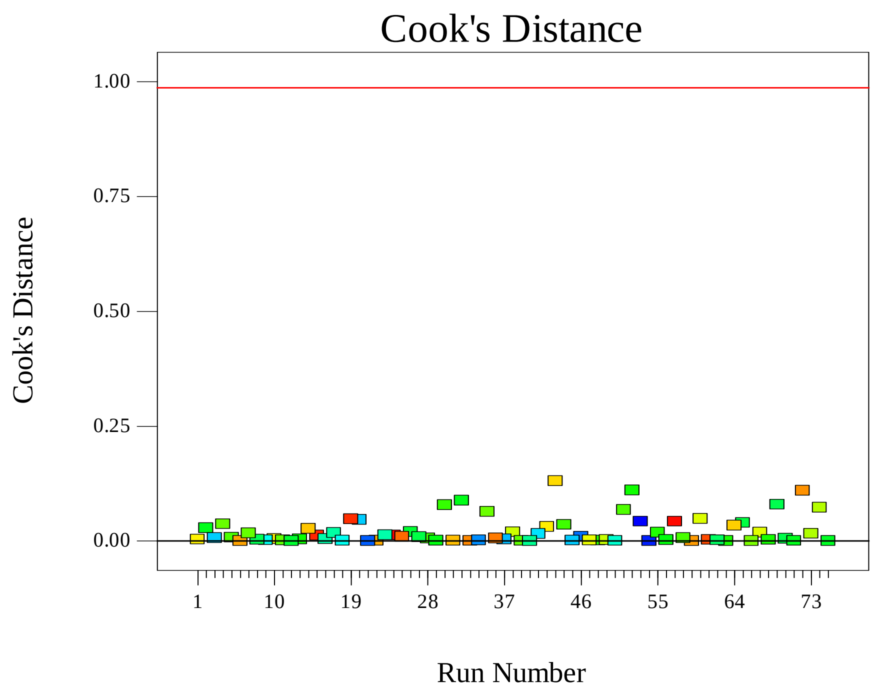
Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	0.28	0.64	0.59	0.52	
2FI	**0.20**	**0.92**	**0.78**	**0.25**	**Suggested**
Quadratic	0.21	0.93	0.76	-0.19	Aliased
Cubic	0.12	1.00	0.93		Aliased

Figure E.9: Diagnostic Charts for the $\ln(SDevV)$ (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
Externally Studentized Residuals
3.64
1.82
0.00
-1.82
-3.64
1
10
19
28
37
46
55
64
73
Run Number


Cook's Distance
Cook's Distance
1.00
0.75
0.50
0.25
0.00
1
10
19
28
37
46
55
64
73
Run Number

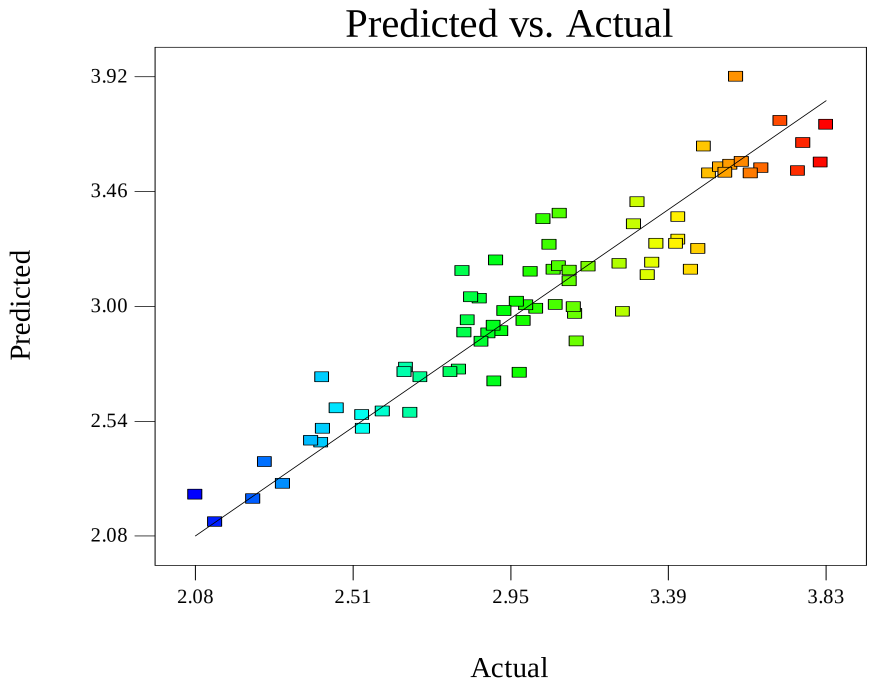
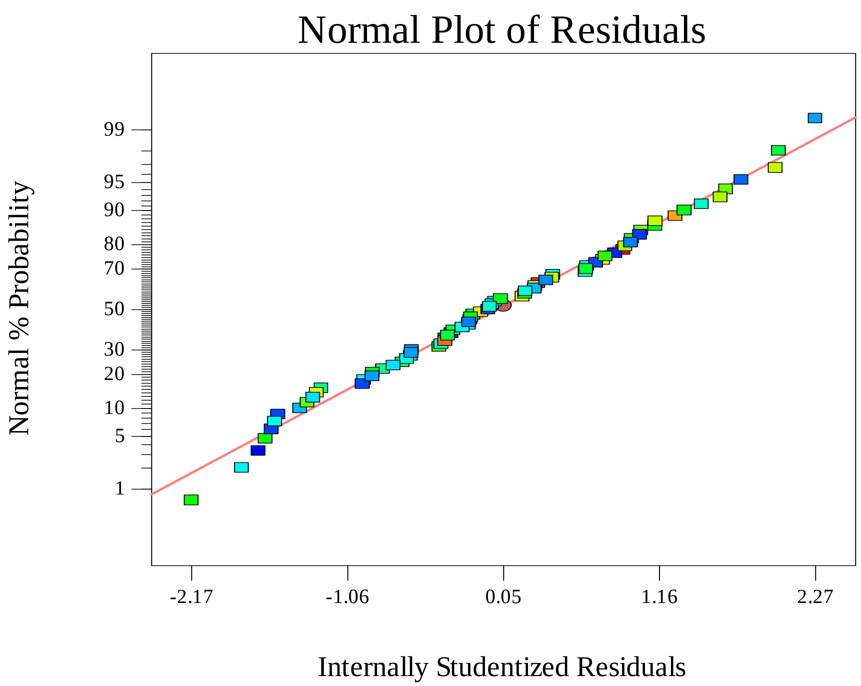
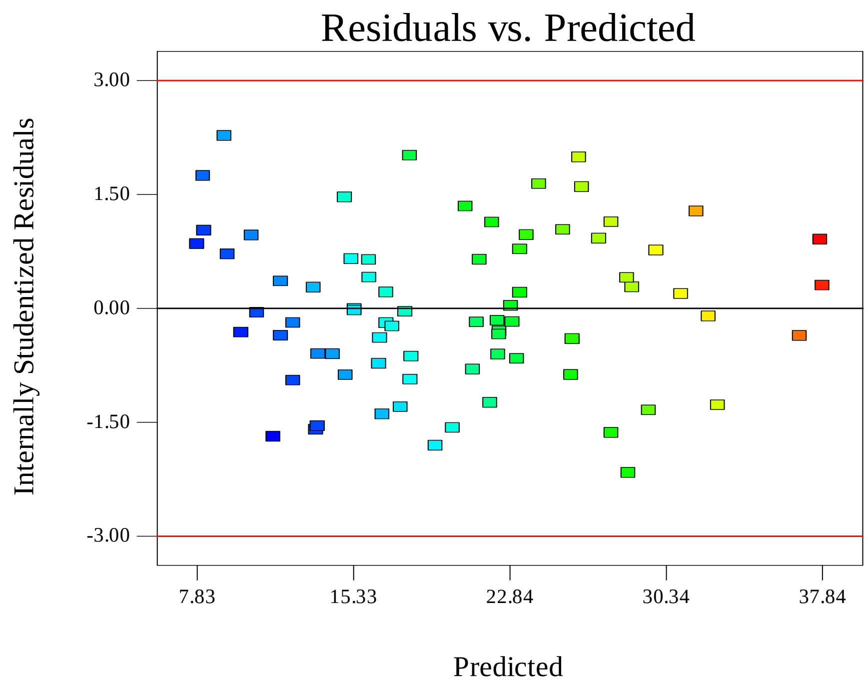

Predicted vs. Actual
Predicted
Actual
3.92
3.46
3.00
2.54
2.08
2.08
2.51
2.95
3.39
3.83

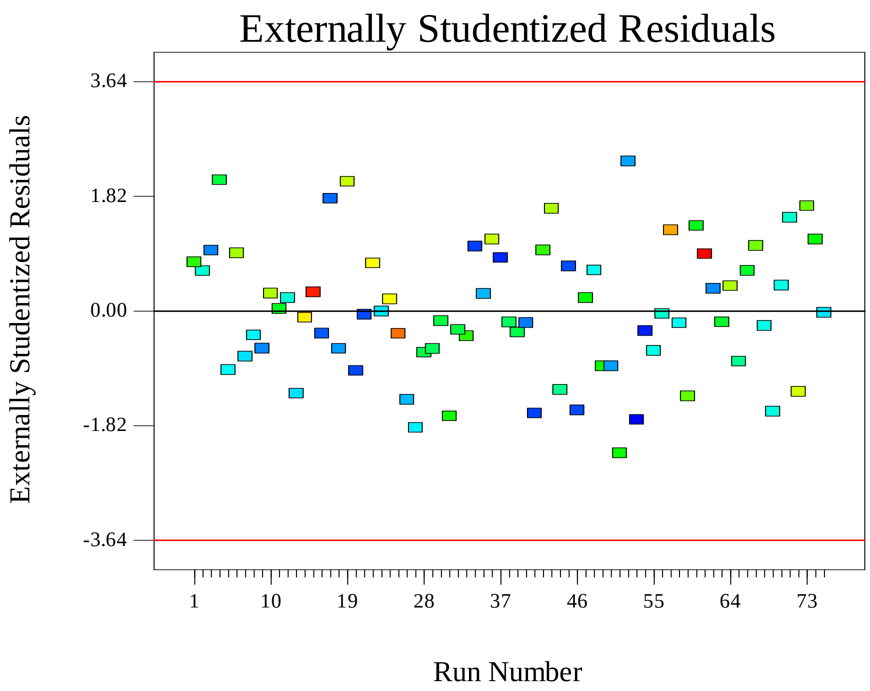
Table E.14: Model Summary Statistics for the SDevS Response

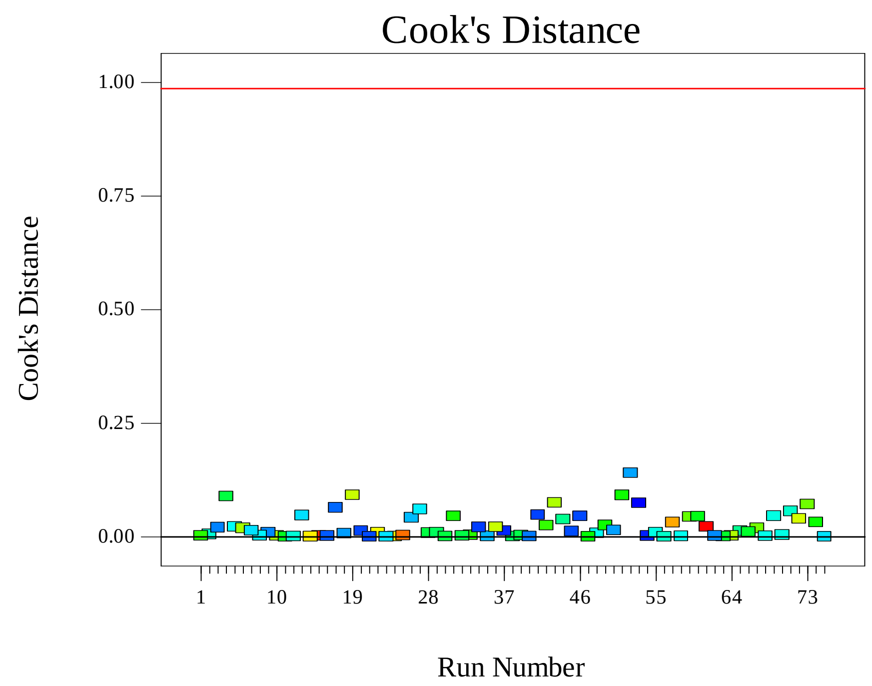
Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	4.78	0.66	0.61	0.54	
2FI	**2.56**	**0.96**	**0.89**	**0.59**	**Suggested**
Quadratic	2.65	0.96	0.88	0.41	Aliased
Cubic	2.17	1.00	0.92		Aliased

Figure E.10: Diagnostic Charts for the SDevS (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
3.64
1.82
0.00
-1.82
-3.64
Externally Studentized Residuals
1
10
19
28
37
46
55
64
73
Run Number


Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
10
19
28
37
46
55
64
73
Run Number

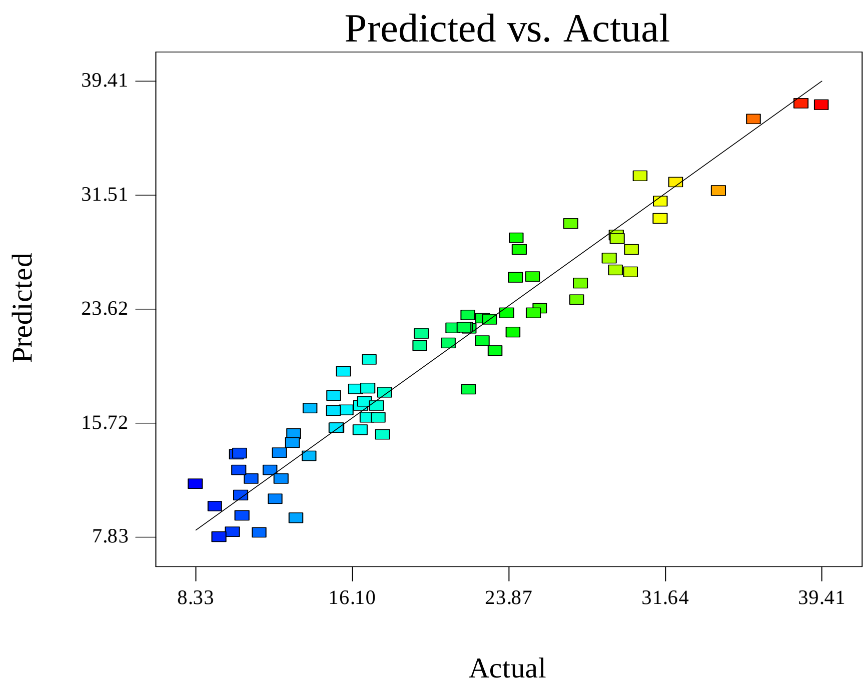
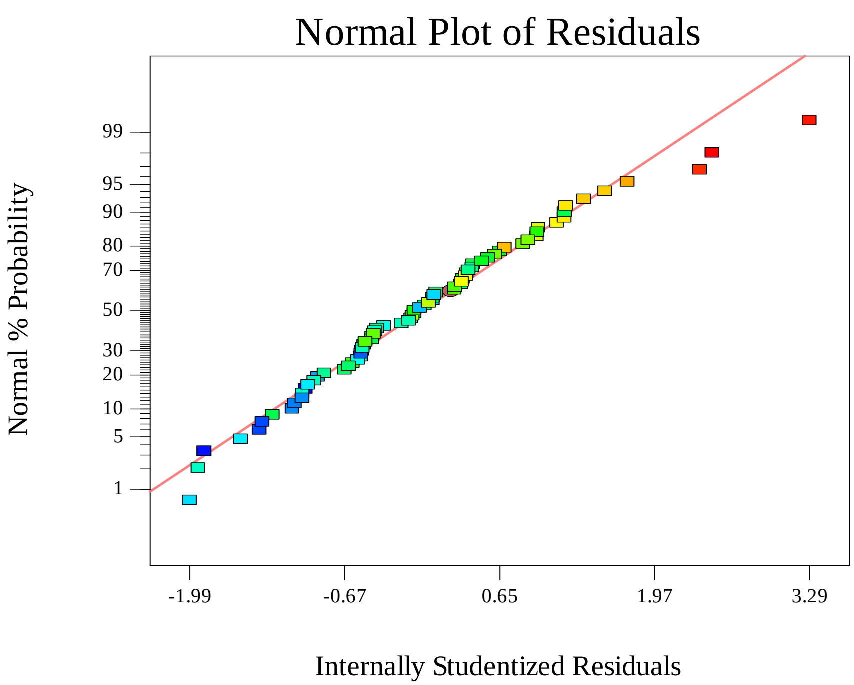
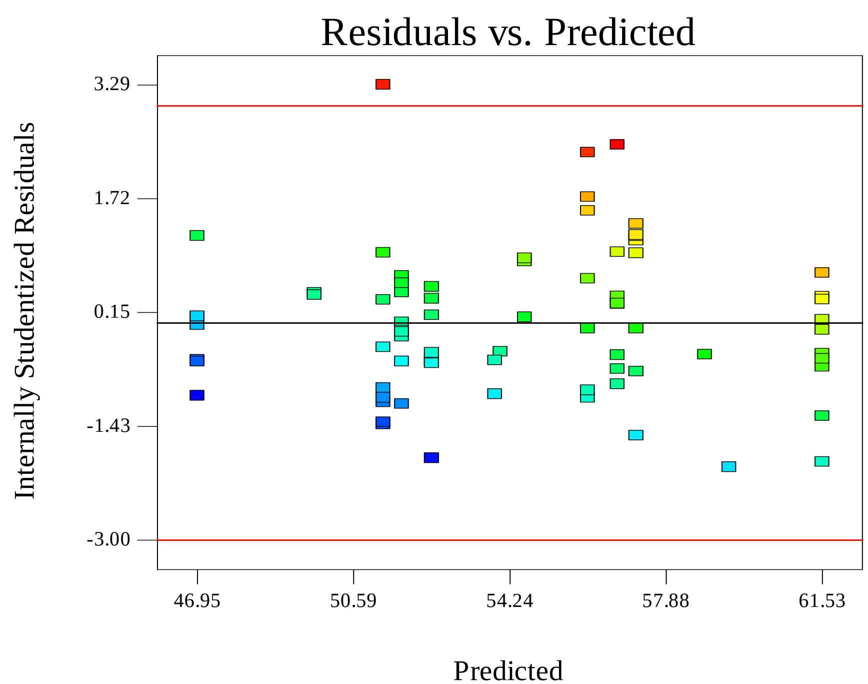

Predicted vs. Actual
39.41
31.51
23.62
15.72
7.83
Predicted
8.33
16.10
23.87
31.64
39.41
Actual

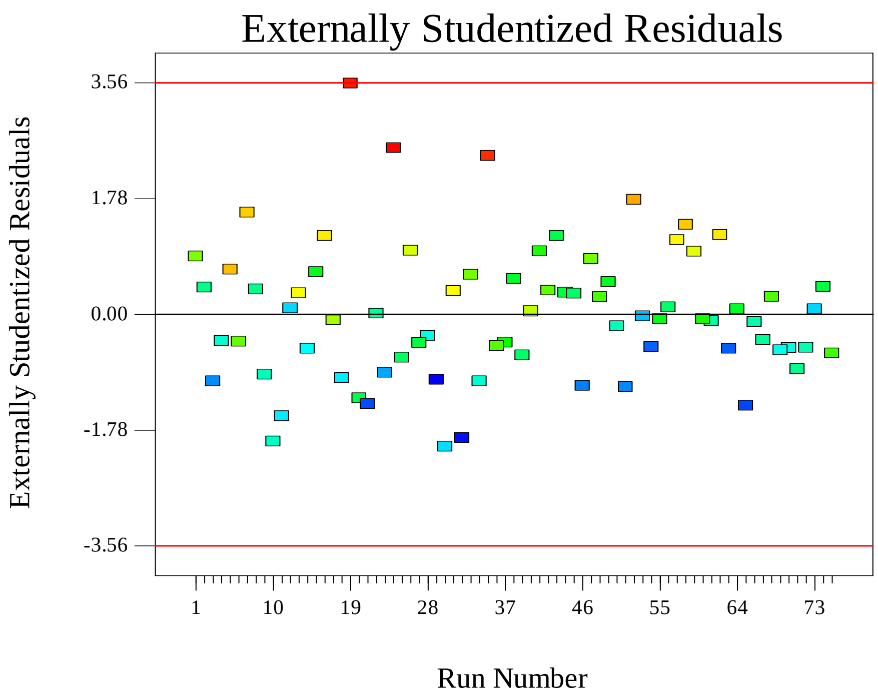
Table E.15: Model Summary Statistics for the CV (VMD) Response

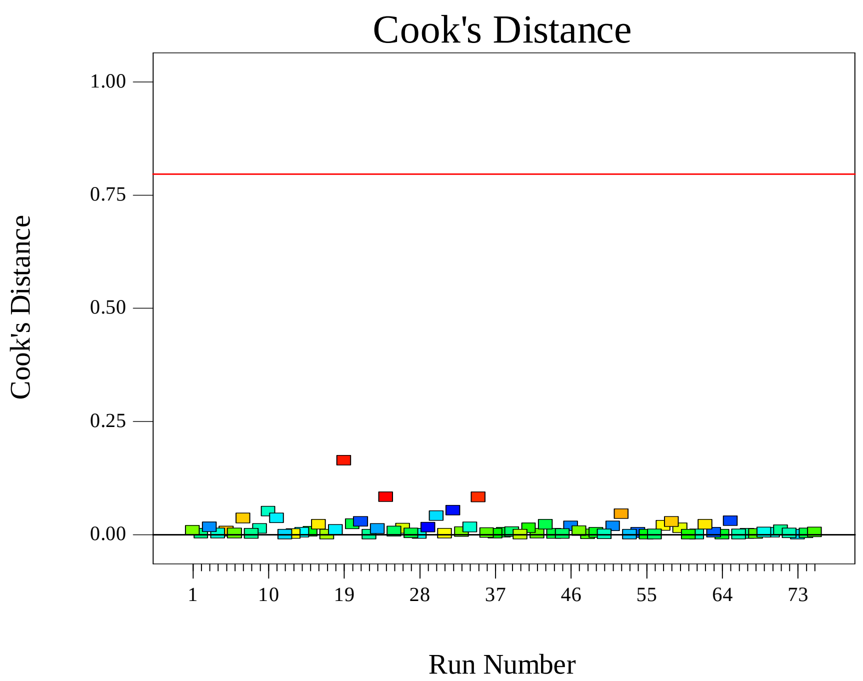
Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	**5.94**	**0.40**	**0.32**	**0.20**	**Suggested**
2FI	6.27	0.70	0.24	-1.35	
Quadratic	6.14	0.78	0.27	-2.29	Aliased
Cubic	3.27	0.99	0.79		Aliased

Figure E.11: Diagnostic Charts for the CV (VMD) (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
3.56
1.78
0.00
-1.78
-3.56
Externally Studentized Residuals
1
10
19
28
37
46
55
64
73
Run Number


Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
10
19
28
37
46
55
64
73
Run Number

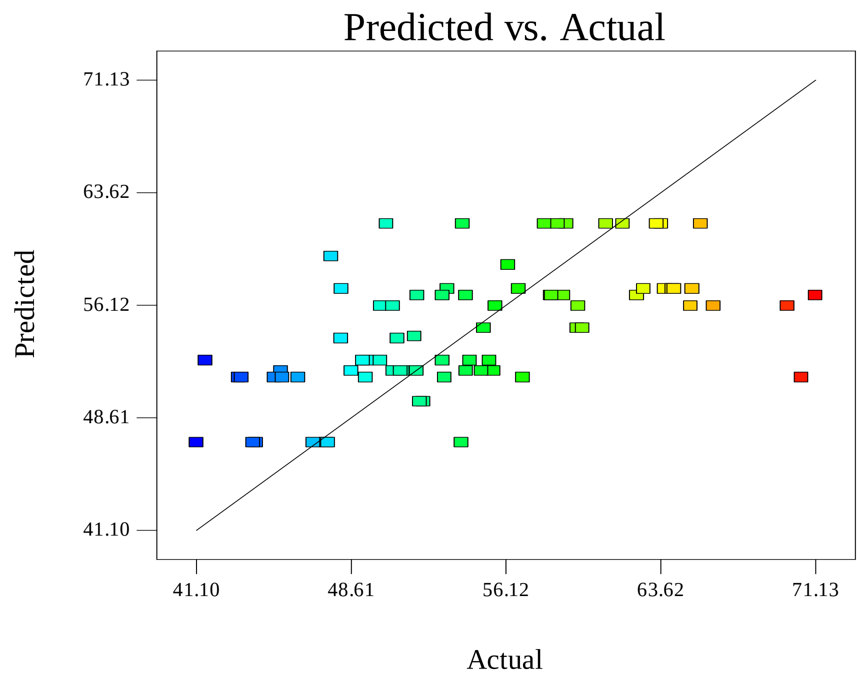
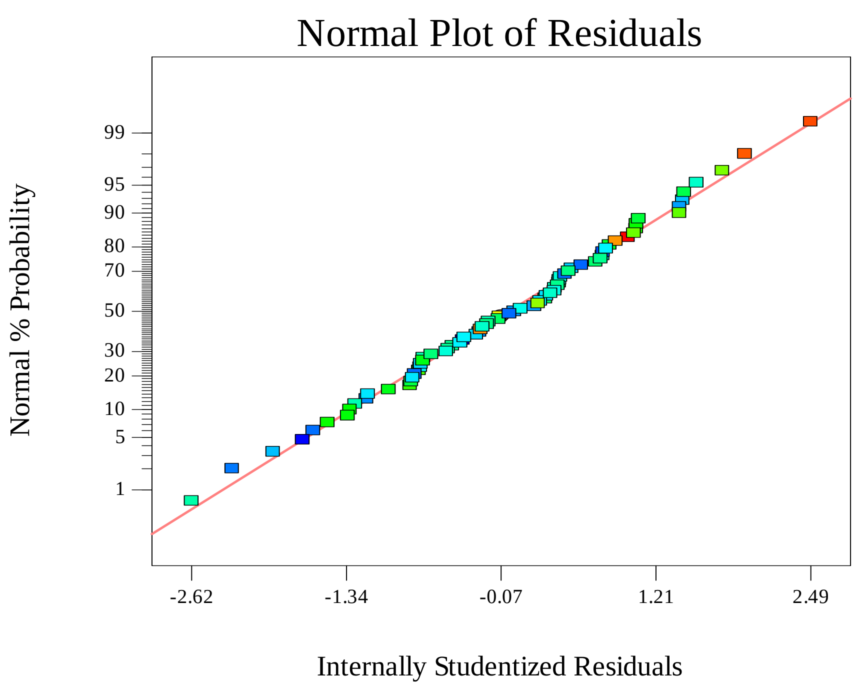
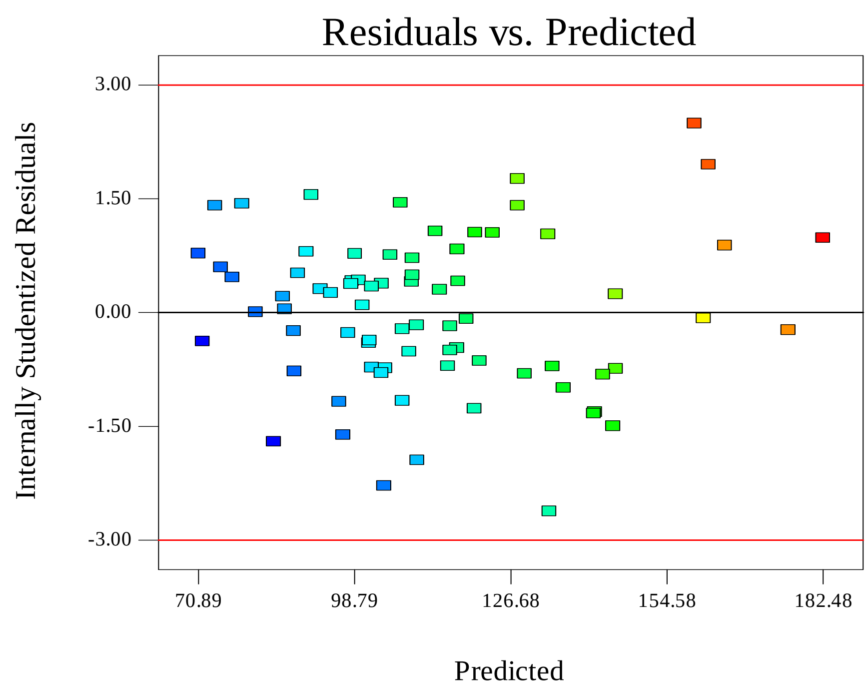

Predicted vs. Actual
Predicted
71.13
63.62
56.12
48.61
41.10
41.10
48.61
56.12
63.62
71.13
Actual

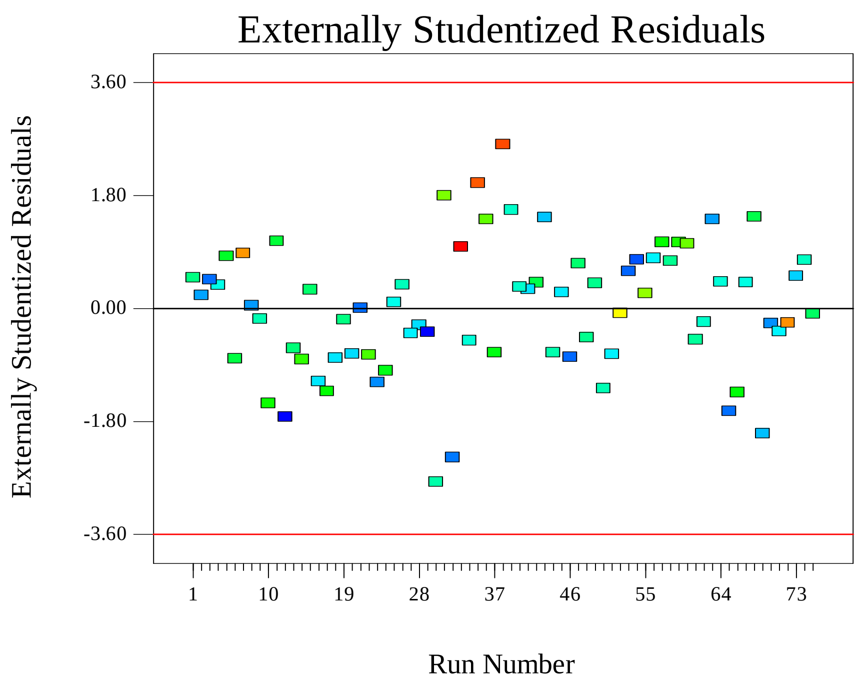
Table E.16: Model Summary Statistics for the CV (SMD) Response

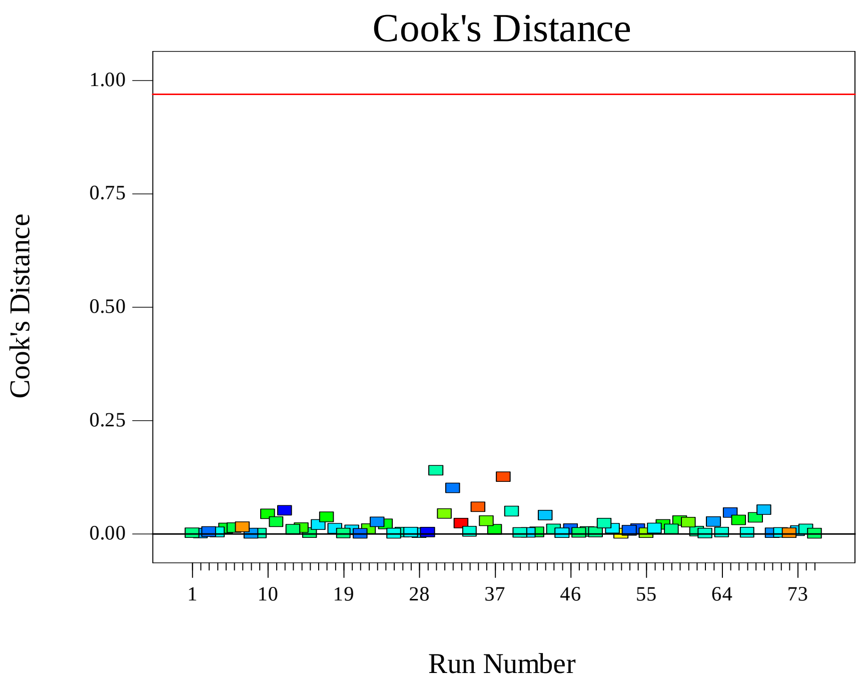
Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	18.83	0.56	0.50	0.41	
2FI	**12.87**	**0.91**	**0.77**	**0.29**	**Suggested**
Quadratic	13.12	0.93	0.76	-0.02	Aliased
Cubic	5.07	1.00	0.96		Aliased

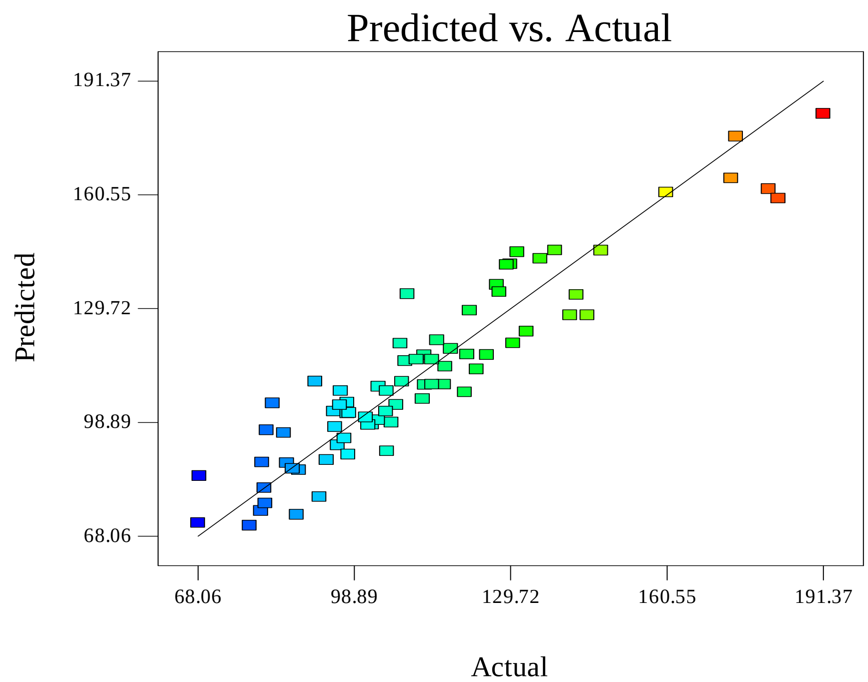
Figure E.12: Diagnostic Charts for the CV (SMD) (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.






Externally Studentized Residuals
3.60
1.80
0.00
-1.80
-3.60
Externally Studentized Residuals
1
10
19
28
37
46
55
64
73
Run Number


Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
10
19
28
37
46
55
64
73
Run Number

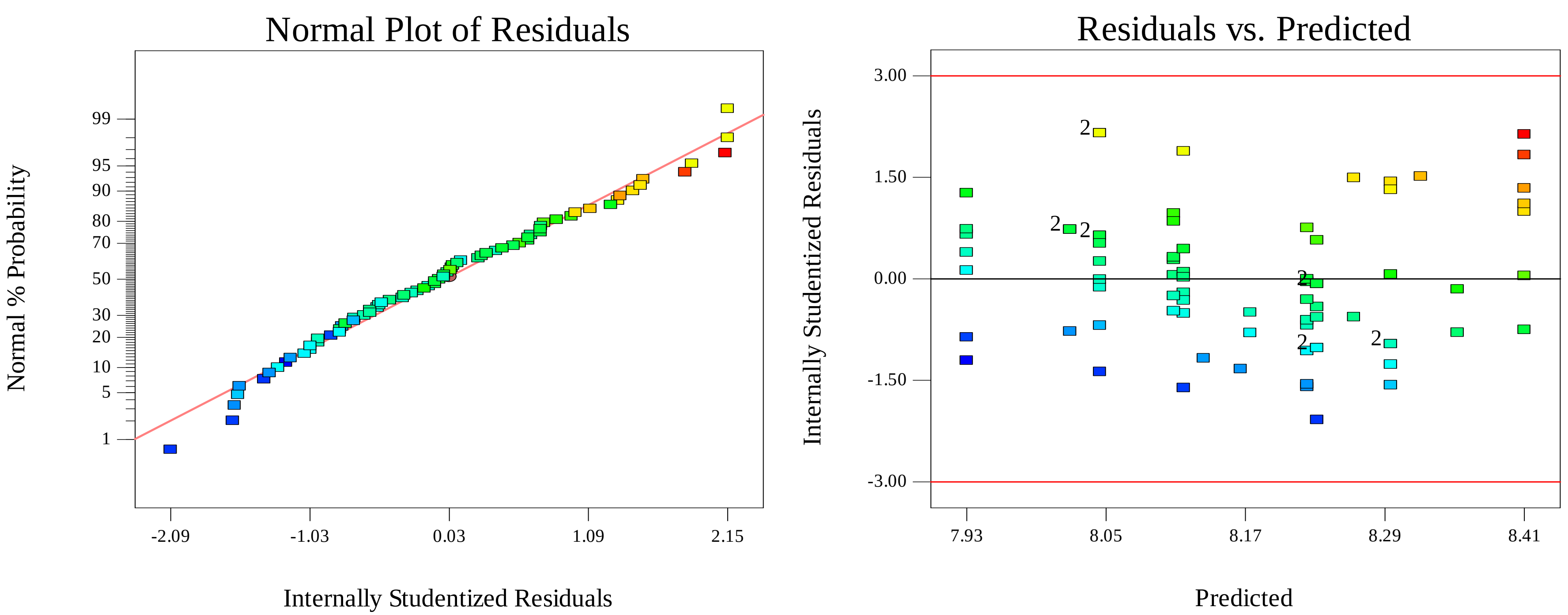


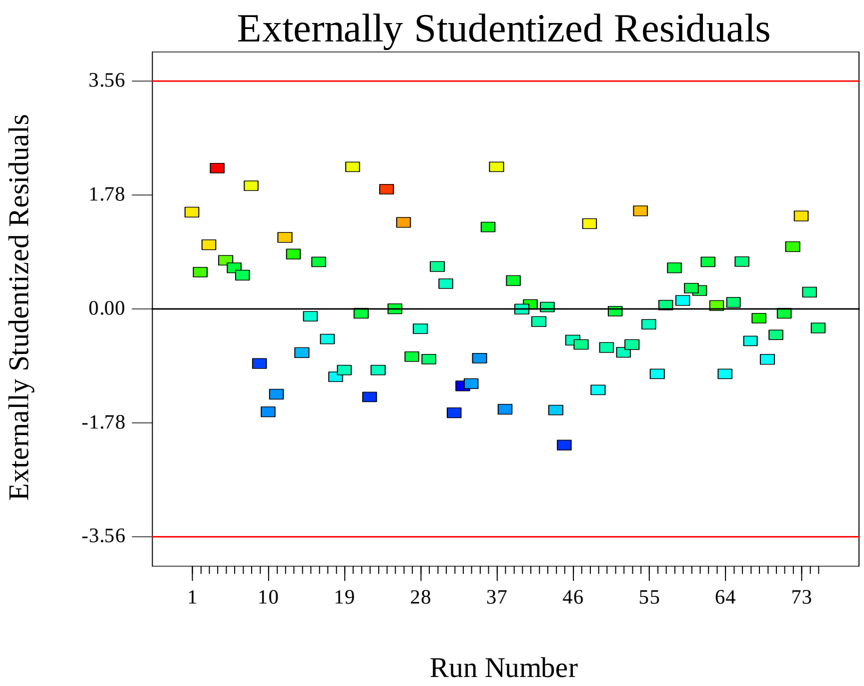
Predicted vs. Actual
191.37
160.55
129.72
98.89
68.06
Predicted
68.06
98.89
129.72
160.55
191.37
Actual

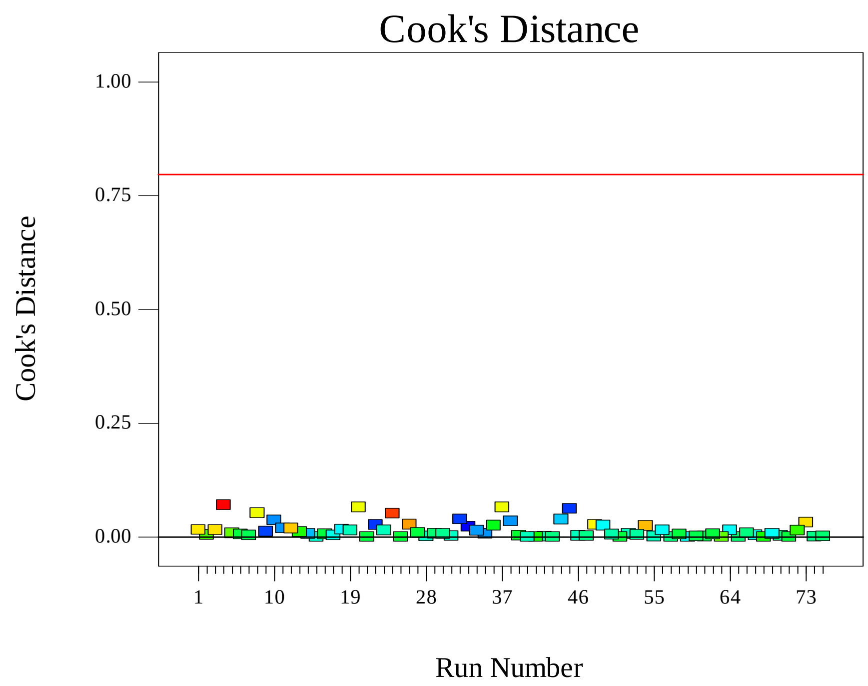
Table E.17: Model Summary Statistics for the pH Response

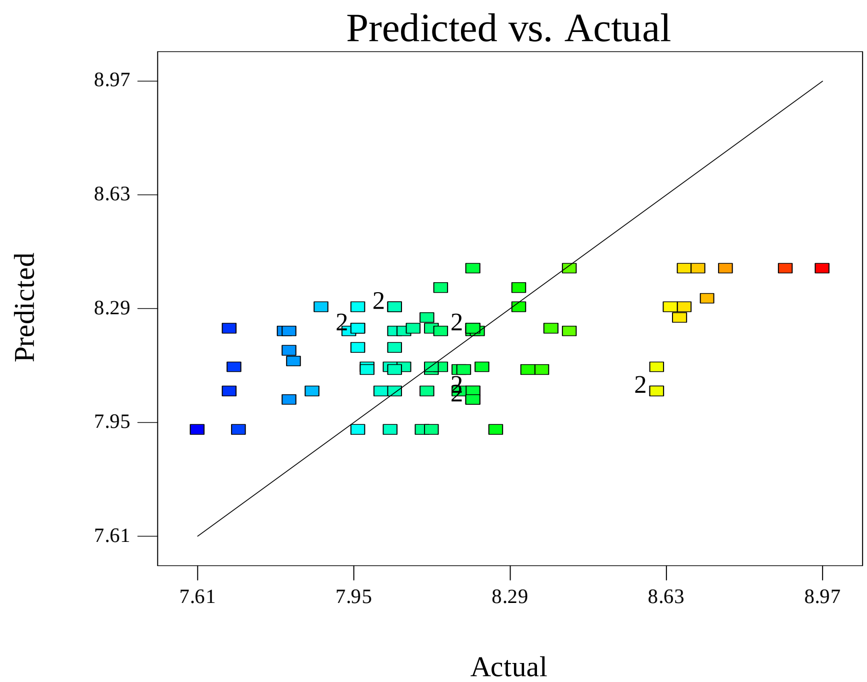
Model	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Notes
Linear	**0.27**	**0.27**	**0.17**	**0.03**	**Suggested**
2FI	0.26	0.70	0.23	-1.24	
Quadratic	0.28	0.75	0.15	-2.19	Aliased
Cubic	0.29	0.95	0.04		Aliased

Figure E.13: Diagnostic Charts for the pH (a) Normal Plot of Residuals, (b) Residuals vs. Predicted Plot, (c) Residuals vs. Run Number, (d) Cook's Distance Plot & (e) Predicted vs. Actual Plot.




Externally Studentized Residuals
3.56
1.78
0.00
-1.78
-3.56
Externally Studentized Residuals
1
10
19
28
37
46
55
64
73
Run Number


Cook's Distance
1.00
0.75
0.50
0.25
0.00
Cook's Distance
1
10
19
28
37
46
55
64
73
Run Number



Predicted vs. Actual
Predicted
Actual
8.97
8.63
8.29
7.95
7.61
7.61
7.95
8.29
8.63
8.97
2
2
2
2
2
2

Appendix E.2 - Response Surface ANOVA

Response **5 VMD**

Backward Elimination Regression with Alpha to Exit = 0.100

Removed	Coefficient Estimate	t for H0 Coeff=0	Prob > |t|	R-Squared	MSE
D-Mass DETA (Organic)	-0.03	-0.04	0.97	0.96	25.30
CD	-0.10	-0.13	0.90	0.96	24.49
CF	-0.15	-0.21	0.84	0.96	23.76
CE	0.18	0.25	0.80	0.96	23.09
BE	0.21	0.30	0.76	0.96	22.47
AF	-0.31	-0.45	0.66	0.96	21.96
EH	-0.36	-0.55	0.59	0.96	21.53
G-Initial Temperature	-0.36	-0.56	0.58	0.96	21.13
FG	-0.45	-0.64	0.52	0.96	20.80
CJ	0.53	0.81	0.43	0.96	20.62
BC	-0.59	-0.91	0.37	0.96	20.53
DF	-0.64	-1.05	0.30	0.96	20.58
AJ	0.60	1.02	0.31	0.95	20.61
DE	0.72	1.10	0.28	0.95	20.71
EF	-0.69	-1.08	0.29	0.95	20.79
GJ	-0.58	-0.99	0.33	0.95	20.77
BF	0.92	1.44	0.16	0.95	21.26
AD	-0.84	-1.35	0.19	0.95	21.63
FH	0.95	1.51	0.14	0.94	22.20
CG	0.87	1.38	0.17	0.94	22.61
BJ	0.79	1.25	0.22	0.94	22.87

Hierarchical Terms Added after Backward Elimination Regression
D-Mass DETA (Organic), G-Initial Temperature

ANOVA for Response Surface Reduced 2FI Model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	17648.25	27	653.6387	27.28531	**< 0.0001**	**significant**
A-Mass Polyester	436.7749	1	436.7749	18.23261	**< 0.0001**	
B-Mass Styrene	1200.735	1	1200.735	50.12313	**< 0.0001**	
C-Mass LMA	1339.613	1	1339.613	55.92042	**< 0.0001**	
D-Mass DETA (Organic)	0.137661	1	0.137661	0.005746	0.93 99	
E-Mass Water	1696.74	1	1696.74	70.82825	**< 0.0001**	
F-Stirrer Speed	2522.784	1	2522.784	105.3104	**< 0.0001**	
G-Initial Temperature	0.090534	1	0.090534	0.003779	0.951 2	
H-Acid Value	808.8206	1	808.8206	33.76318	**< 0.0001**	
J-Viscosity	4350.866	1	4350.866	181.6213	**< 0.0001**	
AB	230.2794	1	230.2794	9.61272	**0.0033**	
AC	145.9063	1	145.9063	6.090672	**0.0173**	
AD	17.26789	1	17.26789	0.720826	0.4002	
AE	68.25657	1	68.25657	2.849283	**0.0980**	
AG	161.3504	1	161.3504	6.735365	**0.0126**	
AH	804.1156	1	804.1156	33.56677	**< 0.0001**	
BD	184.5932	1	184.5932	7.705606	**0.0079**	
BG	612.402	1	612.402	25.56394	**< 0.0001**	
BH	281.055	1	281.055	11.73228	**0.0013**	
CH	156.6507	1	156.6507	6.539182	**0.0138**	
DG	85.386	1	85.386	3.564329	**0.0652**	
DH	108.504	1	108.504	4.529361	**0.0386**	
DJ	92.83581	1	92.83581	3.875312	**0.0549**	
EG	81.86771	1	81.86771	3.417463	**0.0708**	
EJ	118.2283	1	118.2283	4.935289	**0.0312**	
FJ	245.4925	1	245.4925	10.24777	**0.0025**	
GH	94.56173	1	94.56173	3.947358	**0.0528**	
HJ	1719.551	1	1719.551	71.78046	**< 0.0001**	
Residual	1125.918	47	23.9557			
Lack of Fit	1048.197	43	24.37668	1.254579	0.4663	not signi ficant
Pure Error	77.72065	4	19.43016			
Cor Total	18774.16	74				

Std. Dev.	4.894	**R-Squared**	0.940
Mean	41.792	**Adj R-Squai**	0.906
C.V. %	11.711	**Pred R-Squ**	0.839
PRESS	3013.821	**Adeq Precis**	20.550

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	41.68367	1	0.581022	40.51481	42.85254	
A-Mass Polyester	-2.613547	1	0.612077	-3.844887	-1.382207	1.108477
B-Mass Styrene	-4.567494	1	0.645147	-5.865363	-3.269625	1.196746
C-Mass LMA	4.74051	1	0.633928	3.465212	6.015809	1.137143
D-Mass DETA (Organic)	-0.046835	1	0.617835	-1.28976	1.19608 9	1.097564
E-Mass Water	5.394759	1	0.641016	4.105201	6.684316	1.16637 3
F-Stirrer Speed	-7.211937	1	0.702775	-8.625739	-5.798136	1.397553
G-Initial Temperature	-0.037392	1	0.608237	-1.261006	1.18622 3	1.049312
H-Acid Value	3.497233	1	0.60187	2.286426	4.70804	1.133916
J-Viscosity	8.03048	1	0.595879	6.831726	9.229234	1.111454

AB	-2.146188	1	0.692221	-3.538757	-0.75362	1.297751
AC	1.725618	1	0.699217	0.318975	3.132262	1.301803
AD	-0.552561	1	0.650826	-1.861854	0.756732	1.143408
AE	-1.086882	1	0.643895	-2.382231	0.208466	1.099338
AG	-1.706252	1	0.65745	-3.02887	-0.383634	1.154772
AH	3.703183	1	0.639176	2.417327	4.98904	1.210623
BD	1.786862	1	0.643706	0.491892	3.081832	1.124063
BG	-3.296829	1	0.652052	-4.608589	-1.985069	1.134943
BH	-2.169206	1	0.6333	-3.443241	-0.89517	1.154982
CH	-1.588375	1	0.621143	-2.837953	-0.338797	1.094314
DG	1.235909	1	0.654633	-0.081042	2.552861	1.143943
DH	-1.374819	1	0.645992	-2.674387	-0.075251	1.190591
DJ	1.250431	1	0.635194	-0.027415	2.528276	1.160104
EG	-1.294208	1	0.700087	-2.702601	0.114186	1.286494
EJ	1.41068	1	0.634998	0.133229	2.68813	1.140984
FJ	-2.034088	1	0.635412	-3.312371	-0.755805	1.146068
GH	-1.242317	1	0.625287	-2.500232	0.015598	1.108964
HJ	5.148134	1	0.607641	3.925719	6.370549	1.155763

Final Equation in Terms of Coded Factors:

VMD	=	
41.68367		41.68
-2.613547	* A	-2.61
-4.567494	* B	-4.57
4.74051	* C	4.74
-0.046835	* D	-0.05
5.394759	* E	5.39
-7.211937	* F	-7.21
-0.037392	* G	-0.04
3.497233	* H	3.50
8.03048	* J	8.03
-2.146188	* A * B	-2.15
1.725618	* A * C	1.73
-0.552561	* A * D	-0.55
-1.086882	* A * E	-1.09
-1.706252	* A * G	-1.71
3.703183	* A * H	3.70
1.786862	* B * D	1.79
-3.296829	* B * G	-3.30
-2.169206	* B * H	-2.17
-1.588375	* C * H	-1.59
1.235909	* D * G	1.24
-1.374819	* D * H	-1.37
1.250431	* D * J	1.25
-1.294208	* E * G	-1.29
1.41068	* E * J	1.41
-2.034088	* F * J	-2.03
-1.242317	* G * H	-1.24
5.148134	* H * J	5.15

Final Equation in Terms of Actual Factors:

VMD	=
-42.55751	
0.444493	* Mass Polyester
1.134193	* Mass Styrene
-1.307857	* Mass LMA
-23.94173	* Mass DETA (Organic)
0.044234	* Mass Water
0.285663	* Stirrer Speed
7.245392	* Initial Temperature
-4.000607	* Acid Value
-0.120036	* Viscosity
-0.003144	* Mass Polyester * Mass Styrene
0.016077	* Mass Polyester * Mass LMA
-0.016538	* Mass Polyester * Mass DETA (Organic)
-0.000448	* Mass Polyester * Mass Water
-0.005783	* Mass Polyester * Initial Temperature
0.008118	* Mass Polyester * Acid Value
0.121267	* Mass Styrene * Mass DETA (Organic)
-0.025335	* Mass Styrene * Initial Temperature
-0.010783	* Mass Styrene * Acid Value
-0.050208	* Mass LMA * Acid Value
0.194037	* Mass DETA (Organic) * Initial Temperature
-0.139615	* Mass DETA (Organic) * Acid Value
0.007493	* Mass DETA (Organic) * Viscosity
-0.002795	* Mass Water * Initial Temperature
0.000116	* Mass Water * Viscosity
-0.000207	* Stirrer Speed * Viscosity
-0.014286	* Initial Temperature * Acid Value
0.00226	* Acid Value * Viscosity

Response	**1**	**Buildup**		
Transform:	Natural log	Constant:	0.05	

Backward Elimination Regression with Alpha to Exit = 0.100

Removed	**Coefficient Estimate**	**t for H0 Coeff=0**	**Prob > |t|**	**R-Squared**	**MSE**
AC	0.01	-0.05	0.96	0.88	1.07
AJ	0.01	-0.07	0.95	0.88	1.03
BD	0.01	-0.10	0.92	0.88	1.00
AH	0.02	-0.13	0.90	0.88	0.97
CF	-0.02	0.15	0.88	0.88	0.95
AD	-0.02	0.16	0.88	0.88	0.92
CE	0.03	-0.19	0.85	0.88	0.89
DJ	0.02	-0.17	0.86	0.88	0.87
DF	0.04	-0.32	0.75	0.88	0.85
H-Acid Value	0.05	-0.40	0.69	0.88	0.83
BC	0.06	-0.45	0.66	0.88	0.82
HJ	-0.05	0.44	0.66	0.88	0.80
EF	-0.07	0.56	0.58	0.87	0.79
BF	0.08	-0.61	0.55	0.87	0.77
CJ	0.07	-0.59	0.56	0.87	0.76
AB	0.09	-0.75	0.46	0.87	0.76
CG	-0.09	0.79	0.44	0.87	0.75
AF	-0.10	0.84	0.41	0.87	0.74
A-Mass Polyester	-0.09	0.82	0.42	0.87	0.74
FH	0.12	-1.10	0.28	0.86	0.74
F-Stirrer Speed	0.17	-1.45	0.15	0.86	0.76
BJ	-0.16	1.40	0.17	0.85	0.77
DG	-0.16	1.43	0.16	0.84	0.79
AG	0.19	-1.62	0.11	0.84	0.81
FG	0.20	-1.55	0.13	0.83	0.83

Hierarchical Terms Added after Backward Elimination Regression
A-Mass Polyester, F-Stirrer Speed, H-Acid Value

ANOVA for Response Surface Reduced 2FI Mode

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	219.19158	23	9.5300686	11.091876	**< 0.0001**	significant
A-Mass Polyester	0.6290181	1	0.6290181	0.7321029	0.3962	
B-Mass Styrene	63.976589	1	63.976589	74.461205	**< 0.0001**	
C-Mass LMA	5.3864564	1	5.3864564	6.2692001	**0.0155**	
D-Mass DETA (Organic)	9.019256	1	9.019256	10.49735	**0.0021**	
E-Mass Water	7.7185227	1	7.7185227	8.9834503	**0.0042**	
F-Stirrer Speed	0.5245156	1	0.5245156	0.6104743	0.4382	
G-Initial Temperature	6.7457155	1	6.7457155	7.8512173	**0.0072**	
H-Acid Value	0.0195351	1	0.0195351	0.0227366	0.8807	
J-Viscosity	12.288398	1	12.288398	14.302246	**0.0004**	
AE	7.1589033	1	7.1589033	8.3321192	**0.0057**	
BE	5.8004421	1	5.8004421	6.7510306	**0.0122**	
BG	15.886689	1	15.886689	18.490233	**< 0.0001**	
BH	8.4285332	1	8.4285332	9.8098187	**0.0029**	
CD	11.16352	1	11.16352	12.993021	**0.0007**	
CH	11.517019	1	11.517019	13.404452	**0.0006**	
DE	4.8857553	1	4.8857553	5.686443	**0.0209**	
DH	13.424016	1	13.424016	15.623972	**0.0002**	
EG	10.106615	1	10.106615	11.762908	**0.0012**	
EH	6.0581134	1	6.0581134	7.0509296	**0.0105**	
EJ	5.5812131	1	5.5812131	6.4958739	**0.0139**	
FJ	6.2324484	1	6.2324484	7.253835	**0.0096**	
GH	19.595588	1	19.595588	22.806954	**< 0.0001**	
GJ	6.4952388	1	6.4952388	7.559692	**0.0082**	
Residual	43.818872	51	0.8591936			
Lack of Fit	43.739948	47	0.9306372	47.166031	**0.0009**	significant
Pure Error	0.0789244	4	0.0197311			
Cor Total	263.01045	74				

Std. Dev.	0.927	**R-Squared**	0.833
Mean	-0.945	**Adj R-Squa**	0.758
C.V. %	98.116	**Pred R-Squ**	0.654
PRESS	91.054	**Adeq Preci**	11.601

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	-1.070179	1	0.1094677	-1.289944	-0.850413	
A-Mass Polyester	-0.098375	1	0.1149734	-0.329194	0.1324441	1.0905051
B-Mass Styrene	1.0079988	1	0.116814	0.7734848	1.2425127	1.0939364
C-Mass LMA	0.2922601	1	0.1167249	0.0579251	0.5265951	1.0749299
D-Mass DETA (Organic)	0.3857457	1	0.1190587	0.1467253	0.624766	1.1363825

E-Mass Water	-0.356784	1	0.1190374	-0.595761	-0.117806	1.1214622
F-Stirrer Speed	0.0954032	1	0.1221038	-0.14973	0.3405367	1.176282
G-Initial Temperature	-0.327103	1	0.116739	-0.561466	-0.09274	1.077727
H-Acid Value	0.0173923	1	0.1153438	-0.21417	0.2489547	1.1611327
J-Viscosity	-0.421992	1	0.1115841	-0.646007	-0.197978	1.0866698
AE	0.3518931	1	0.1219082	0.1071521	0.5966341	1.0987162
BE	-0.319321	1	0.1228973	-0.566048	-0.072594	1.1213052
BG	0.5221039	1	0.1214187	0.2783456	0.7658622	1.0972317
BH	0.3646832	1	0.1164355	0.1309293	0.5984371	1.0885406
CD	0.4499326	1	0.1248223	0.1993412	0.7005239	1.159609
CH	-0.430491	1	0.1175818	-0.666547	-0.194436	1.0933447
DE	0.3048325	1	0.1278324	0.0481983	0.5614667	1.2172247
DH	0.4772656	1	0.1207437	0.2348626	0.7196687	1.1597254
EG	-0.45625	1	0.1330287	-0.723316	-0.189183	1.2951258
EH	-0.321544	1	0.1210925	-0.564648	-0.078441	1.1568791
EJ	0.3048589	1	0.1196135	0.0647248	0.5449929	1.1287904
FJ	-0.322069	1	0.119582	-0.56214	-0.081999	1.1317467
GH	0.5566871	1	0.1165675	0.322668	0.7907061	1.0745635
GJ	-0.329438	1	0.119818	-0.569983	-0.088894	1.1353278

Final Equation in Terms of Coded Factors

Ln(Buildup -	=
-1.070179	
-0.098375	* A
1.0079988	* B
0.2922601	* C
0.3857457	* D
-0.356784	* E
0.0954032	* F
-0.327103	* G
0.0173923	* H
-0.421992	* J
0.3518931	* A * E
-0.319321	* B * E
0.5221039	* B * G
0.3646832	* B * H
0.4499326	* C * D
-0.430491	* C * H
0.3048325	* D * E
0.4772656	* D * H
-0.45625	* E * G
-0.321544	* E * H
0.3048589	* E * J
-0.322069	* F * J
0.5566871	* G * H
-0.329438	* G * J

Final Equation in Terms of Actual Factors

Ln(Buildup -	=
50.380582	
-0.15158	* Mass Polyester
0.2088574	* Mass Styrene
-0.224206	* Mass LMA
-9.933756	* Mass DETA (Organic)
-0.053563	* Mass Water
0.069977	* Stirrer Speed
0.7383367	* Initial Temperature
0.0898066	* Acid Value
-0.011502	* Viscosity
0.0001449	* Mass Polyester * Mass Water
-0.000298	* Mass Styrene * Mass Water
0.0040123	* Mass Styrene * Initial Temperature
0.0018128	* Mass Styrene * Acid Value
0.1941775	* Mass LMA * Mass DETA (Organic)
-0.013608	* Mass LMA * Acid Value
0.0058142	* Mass DETA (Organic) * Mass Water
0.0484672	* Mass DETA (Organic) * Acid Value
-0.000985	* Mass Water * Initial Temperature
-0.000449	* Mass Water * Acid Value
2.513E-05	* Mass Water * Viscosity
-3.28E-05	* Stirrer Speed * Viscosity
0.0064015	* Initial Temperature * Acid Value
-0.000224	* Initial Temperature * Viscosity

Response **2 SG**

Backward Elimination Regression with Alpha to Exit = 0.100

Removed	**Coefficient Estimate**	**t for H0 Coeff=0**	**Prob > |t|**	**R-Squared**	**MSE**
AB	0.00	-0.03	0.98	0.81	0.00
BC	0.00	-0.06	0.96	0.81	0.00
FH	0.00	0.06	0.95	0.81	0.00
CG	0.00	0.07	0.95	0.81	0.00
BJ	0.00	-0.15	0.88	0.81	0.00
FJ	0.00	-0.16	0.87	0.81	0.00
D-Mass DI	0.00	-0.17	0.86	0.81	0.00
AD	0.00	-0.19	0.85	0.81	0.00
G-Initial Te	0.00	0.20	0.84	0.81	0.00
DH	0.00	0.24	0.81	0.81	0.00
FG	0.00	0.27	0.79	0.81	0.00
DG	0.00	-0.30	0.77	0.81	0.00
AH	0.00	0.29	0.77	0.81	0.00
CH	0.00	0.29	0.78	0.81	0.00
BE	0.00	0.36	0.72	0.81	0.00
GJ	0.00	0.48	0.63	0.81	0.00
BF	0.00	0.58	0.56	0.80	0.00
DJ	0.00	-0.56	0.58	0.80	0.00
H-Acid Val	0.00	-0.57	0.57	0.80	0.00
J-Viscosity	0.00	-0.74	0.47	0.80	0.00
DE	0.00	-0.72	0.48	0.80	0.00
BG	0.00	0.75	0.46	0.80	0.00
EG	0.00	0.79	0.43	0.79	0.00
B-Mass Sty	0.00	1.04	0.30	0.79	0.00
BH	0.00	1.10	0.28	0.78	0.00
CJ	0.00	-1.27	0.21	0.78	0.00
AF	0.00	-1.05	0.30	0.77	0.00
BD	0.00	1.36	0.18	0.76	0.00
EJ	0.00	-1.42	0.16	0.76	0.00
HJ	0.00	1.50	0.14	0.75	0.00
AC	0.00	1.48	0.14	0.74	0.00
AE	0.00	1.67	0.10	0.72	0.00

Hierarchical Terms Added after Backward Eliminati on Regression

D-Mass DETA (Organic), G-Initial Temperature, H -Acid Value, J-Viscosity

ANOVA for Response Surface Reduced 2FI Mode l

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.002447	17	0.000144	8.894879	**< 0.0001**	significant
A-Mass Pc	0.001014	1	0.001014	62.65286	**< 0.0001**	
C-Mass LN	6.8E-05	1	6.8E-05	4.200358	**0.0452**	
D-Mass DI	2E-07	1	2E-07	0.012376	0.9118	
E-Mass Wa	0.000346	1	0.000346	21.38018	**< 0.0001**	
F-Stirrer Sp	0.00013	1	0.00013	8.02486	**0.0064**	
G-Initial Te	7.46E-06	1	7.46E-06	0.46072	0.5001	
H-Acid Val	2.11E-05	1	2.11E-05	1.304442	0.2584	
J-Viscosity	6.23E-06	1	6.23E-06	0.384742	0.5376	
AG	0.000117	1	0.000117	7.225237	**0.0095**	
AJ	7.42E-05	1	7.42E-05	4.582665	**0.0367**	
CD	0.00011	1	0.00011	6.781083	**0.0118**	
CE	6.47E-05	1	6.47E-05	3.998286	**0.0505**	
CF	0.000123	1	0.000123	7.625923	**0.0078**	
DF	0.000132	1	0.000132	8.137583	**0.0061**	
EF	5.01E-05	1	5.01E-05	3.096864	**0.0840**	
EH	5.1E-05	1	5.1E-05	3.154034	**0.0813**	
GH	8.77E-05	1	8.77E-05	5.420065	**0.0236**	
Residual	0.00089	55	1.62E-05			
Lack of Fit	0.000886	51	1.74E-05	15.60835	**0.0078**	significant
Pure Error	4.45E-06	4	1.11E-06			
Cor Total	0.003337	72				

Std. Dev.	0.004	**R-Squared**	0.733
Mean	1.045	**Adj R-Squa**	0.651
C.V. %	0.385	**Pred R-Squ**	0.522

PRESS	0.002	**Adeq Precis**	14.017

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	1.04548	1	0.000479	1.044519	1.04644	
A-Mass Pol	0.00393	1	0.000497	0.002935	0.004925	1.065726
C-Mass LM.	-0.001049	1	0.000512	-0.002075	-2.33E-05	1.061098
D-Mass DE	-5.76E-05	1	0.000518	-0.001095	0.00098	1.109352
E-Mass Wat	-0.002384	1	0.000515	-0.003417	-0.00135	1.083768
F-Stirrer Spe	-0.001478	1	0.000522	-0.002524	-0.000432	1.109342
G-Initial Ter	0.000367	1	0.00054	-0.000716	0.00145	1.191423
H-Acid Valu	-0.000549	1	0.000481	-0.001513	0.000415	1.042024
J-Viscosity	-0.0003	1	0.000483	-0.001267	0.000668	1.05188 9
AG	-0.001457	1	0.000542	-0.002544	-0.000371	1.144327
AJ	-0.001077	1	0.000503	-0.002085	-6.88E-05	1.093947
CD	-0.001383	1	0.000531	-0.002447	-0.000319	1.080372
CE	-0.001067	1	0.000533	-0.002136	2.39E-06	1.066544
CF	-0.001505	1	0.000545	-0.002596	-0.000413	1.112626
DF	-0.001517	1	0.000532	-0.002583	-0.000451	1.08009
EF	0.000994	1	0.000565	-0.000138	0.002126	1.199726
EH	0.000961	1	0.000541	-0.000123	0.002046	1.191099
GH	-0.00118	1	0.000507	-0.002195	-0.000164	1.047339

Final Equation in Terms of Coded Factors:

SG	=	
1.04548		1.04548
0.00393	* A	3.93E-03
-0.001049	* C	-1.05E-03
-5.76E-05	* D	-5.76E-05
-0.002384	* E	-2.38E-03
-0.001478	* F	-1.48E-03
0.000367	* G	3.67E-04
-0.000549	* H	-5.49E-04
-0.0003	* J	-3.00E-04
-0.001457	* A * G	-1.46E-03
-0.001077	* A * J	-1.08E-03
-0.001383	* C * D	-1.38E-03
-0.001067	* C * E	-1.07E-03
-0.001505	* C * F	-1.50E-03
-0.001517	* D * F	-1.52E-03
0.000994	* E * F	9.94E-04
0.000961	* E * H	9.61E-04
-0.00118	* G * H	-1.18E-03

Final Equation in Terms of Actual Factors:

SG	=
0.879203	
0.0005	* Mass Polyester
0.012525	* Mass LMA
0.02058	* Mass DETA (Organic)
-0.000114	* Mass Water
-5.86E-05	* Stirrer Speed
0.002035	* Initial Temperature
-0.001124	* Acid Value
4.06E-05	* Viscosity
-4.94E-06	* Mass Polyester * Initial Temperature
-1.39E-07	* Mass Polyester * Viscosity
-0.000597	* Mass LMA * Mass DETA (Organic)
-6.33E-06	* Mass LMA * Mass Water
-1.1E-05	* Mass LMA * Stirrer Speed
-3.57E-05	* Mass DETA (Organic) * Stirrer Speed
3.22E-07	* Mass Water * Stirrer Speed
1.34E-06	* Mass Water * Acid Value
-1.36E-05	* Initial Temperature * Acid Value

Response **3 %NVC**

Backward Elimination Regression with Alpha to Exit = 0.100

Removed	Coefficient Estimate	t for H0 Coeff=0	Prob > |t|	R-Squared	MSE
C-Mass LMA	0.06	1.29	0.20	0.95	0.16

ANOVA for Response Surface Reduced Linear M odel

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	220.2146	8	27.52682	167.9683	**< 0.0001**	significant
A-Mass Polyester	144.3649	1	144.3649	880.9124	**< 0.0001**	
B-Mass Styrene	21.97624	1	21.97624	134.0987	**< 0.0001**	
D-Mass DETA (Organic)	2.142575	1	2.142575	13.07396	**0.0006**	
E-Mass Water	52.24592	1	52.24592	318.8038	**< 0.0001**	
F-Stirrer Speed	0.884455	1	0.884455	5.396932	**0.0233**	
G-Initial Temperature	0.590159	1	0.590159	3.60114	**0.0622**	
H-Acid Value	11.58342	1	11.58342	70.68184	**< 0.0001**	
J-Viscosity	0.542482	1	0.542482	3.310219	**0.0735**	
Residual	10.65227	65	0.163881			
Lack of Fit	9.704372	61	0.159088	0.671328	0.7835	not sign ificant
Pure Error	0.9479	4	0.236975			
Cor Total	230.8669	73				

Std. Dev.	0.405	**R-Squared**	0.954
Mean	24.989	**Adj R-Squa**	0.948
C.V. %	1.620	**Pred R-Squ**	0.940
PRESS	13.767	**Adeq Precis**	51.450

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	25.05104	1	0.047424	24.95632	25.14575	
A-Mass Polyester	1.463152	1	0.049297	1.364699	1.561606	1.0 34837
B-Mass Styrene	0.577797	1	0.049896	0.478148	0.677445	1.032 192
D-Mass DETA (Organic)	0.179967	1	0.049773	0.080565	0.2793 7	1.024653
E-Mass Water	-0.894084	1	0.050075	-0.99409	-0.794078	1.024 924
F-Stirrer Speed	-0.117528	1	0.05059	-0.218563	-0.016492	1 .041079
G-Initial Temperature	0.094353	1	0.04972	-0.004946	0.193 651	1.008843
H-Acid Value	-0.399332	1	0.047499	-0.494193	-0.304471	1.0 1874
J-Viscosity	-0.086201	1	0.047379	-0.180823	0.008421	1.013 608

Final Equation in Terms of Coded Factors:

%NVC	=	
25.05104		25.051
1.463152	* A	1.463
0.577797	* B	0.578
0.179967	* D	0.180
-0.894084	* E	-0.894
-0.117528	* F	-0.118
0.094353	* G	0.094
-0.399332	* H	-0.399
-0.086201	* J	-0.086

Final Equation in Terms of Actual Factors:

%NVC	=
26.64444	
0.037192	* Mass Polyester
0.033302	* Mass Styrene
0.21191	* Mass DETA (Organic)
-0.014483	* Mass Water
-0.002351	* Stirrer Speed
0.01258	* Initial Temperature
-0.03444	* Acid Value
-0.000439	* Viscosity

Response	**10 Viscosity**		
Transform:	Inverse sqr	Constant:	0

Backward Elimination Regression with Alpha to Exit = 0.100

Removed	**Coefficient Estimate**	**t for H0 Coeff=0**	**Prob > |t|**	**R-Squared**	**MSE**
CG	0.00	0.05	0.96	0.93	0.00
BD	0.00	-0.07	0.94	0.93	0.00
DF	0.00	-0.12	0.90	0.93	0.00
CF	0.00	-0.29	0.77	0.93	0.00
B^2	0.00	0.26	0.80	0.93	0.00
F-Stirrer Speed	0.00	-0.19	0.85	0.93	0.00
EJ	0.00	0.23	0.82	0.93	0.00
FG	0.00	0.42	0.67	0.93	0.00
AG	0.00	0.54	0.59	0.93	0.00
EH	0.00	0.57	0.57	0.93	0.00
DJ	0.00	-0.60	0.55	0.92	0.00
BF	0.00	0.77	0.45	0.92	0.00
DG	0.00	0.98	0.33	0.92	0.00
CJ	0.00	-1.03	0.31	0.92	0.00
BG	0.00	-1.04	0.31	0.92	0.00
EG	0.00	-0.93	0.36	0.91	0.00
CD	0.00	1.27	0.21	0.91	0.00
AE	0.00	1.28	0.21	0.91	0.00
A^2	0.00	-1.25	0.22	0.90	0.00
CH	0.00	1.09	0.28	0.90	0.00
F^2	0.00	-1.21	0.23	0.90	0.00
G-Initial Temperature	0.00	1.13	0.27	0.89	0.00
BJ	0.00	-1.31	0.20	0.89	0.00
AF	0.00	1.20	0.24	0.88	0.00
GJ	0.00	-1.29	0.20	0.88	0.00
E^2	0.00	1.14	0.26	0.88	0.00
BE	0.00	-1.48	0.15	0.87	0.00
D^2	0.00	-1.63	0.11	0.86	0.00

Hierarchical Terms Added after Backward Elimination Regression
F-Stirrer Speed, G-Initial Temperature

ANOVA for Response Surface Reduced Quadratic Model

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.007527	26	0.00029	11.21833	**< 0.0001**	significant
A-Mass Polyester	0.001029	1	0.001029	39.87607	**< 0.0001**	
B-Mass Styrene	0.000793	1	0.000793	30.73949	**< 0.0001**	
C-Mass LMA	0.000638	1	0.000638	24.72051	**< 0.0001**	
D-Mass DETA (Organic)	0.000864	1	0.000864	33.47049	**< 0.0001**	
E-Mass Water	0.000377	1	0.000377	14.60592	**0.0004**	
F-Stirrer Speed	3.19E-06	1	3.19E-06	0.123618	0.7267	
G-Initial Temperature	2.42E-06	1	2.42E-06	0.093864	0.7607	
H-Acid Value	0.000101	1	0.000101	3.922571	**0.0536**	
J-Viscosity	0.000181	1	0.000181	7.021374	**0.0110**	
AB	7.71E-05	1	7.71E-05	2.988279	**0.0906**	
AC	9.99E-05	1	9.99E-05	3.872116	**0.0551**	
AD	0.000104	1	0.000104	4.046148	**0.0502**	
AH	0.000589	1	0.000589	22.81628	**< 0.0001**	
AJ	0.000221	1	0.000221	8.579637	**0.0053**	
BC	9.01E-05	1	9.01E-05	3.492774	**0.0680**	
BH	0.000216	1	0.000216	8.372357	**0.0058**	
CE	8.65E-05	1	8.65E-05	3.351778	**0.0736**	
DE	9.46E-05	1	9.46E-05	3.665673	**0.0618**	
DH	0.000663	1	0.000663	25.69214	**< 0.0001**	
EF	0.000153	1	0.000153	5.932551	**0.0188**	
FH	9.66E-05	1	9.66E-05	3.741788	**0.0592**	
FJ	0.000117	1	0.000117	4.543322	**0.0384**	
GH	0.001251	1	0.001251	48.47375	**< 0.0001**	
HJ	0.000962	1	0.000962	37.28996	**< 0.0001**	
C^2	6.75E-05	1	6.75E-05	2.617336	**0.1125**	
G^2	0.000135	1	0.000135	5.246048	**0.0266**	
Residual	0.001187	46	2.58E-05			
Lack of Fit	0.001155	42	2.75E-05	3.444413	0.1174	not significant
Pure Error	3.19E-05	4	7.98E-06			
Cor Total	0.008714	72				

Std. Dev.	0.005	**R-Squared**	0.864
Mean	0.032	**Adj R-Squa**	0.787
C.V. %	16.006	**Pred R-Squ**	0.651
PRESS	0.003	**Adeq Preci**	14.622

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	0.033154	1	0.002777	0.027563	0.038744	
A-Mass Polyester	0.004256	1	0.000674	0.0029	0.005613	1.214503
B-Mass Styrene	-0.003786	1	0.000683	-0.005161	-0.002412	1.20871
C-Mass LMA	-0.003393	1	0.000683	-0.004767	-0.00202	1.182448
D-Mass DETA (Organic)	-0.003746	1	0.000648	-0.00505	-0.002443	1.088379

E-Mass Water	0.002607	1	0.000682	0.001234	0.003979	1.189612
F-Stirrer Speed	-0.000253	1	0.00072	-0.001702	0.001196	1.3202
G-Initial Temperature	0.000208	1	0.000679	-0.001159	0.001576	1.180482
H-Acid Value	0.001331	1	0.000672	-2.17E-05	0.002684	1.276101
J-Viscosity	0.001733	1	0.000654	0.000416	0.003049	1.209175
AB	0.001278	1	0.000739	-0.00021	0.002766	1.331386
AC	0.001458	1	0.000741	-3.34E-05	0.00295	1.318633
AD	0.001413	1	0.000703	-9.78E-07	0.002827	1.20262
AH	-0.003308	1	0.000692	-0.004702	-0.001914	1.281951
AJ	0.001931	1	0.000659	0.000604	0.003258	1.16005
BC	-0.001349	1	0.000722	-0.002803	0.000104	1.248197
BH	-0.001916	1	0.000662	-0.003248	-0.000583	1.137588
CE	0.001279	1	0.000698	-0.000127	0.002685	1.146606
DE	-0.001352	1	0.000706	-0.002773	6.94E-05	1.197928
DH	0.003605	1	0.000711	0.002174	0.005037	1.291744
EF	-0.001784	1	0.000732	-0.003258	-0.00031	1.267614
FH	-0.001347	1	0.000696	-0.002749	5.47E-05	1.236482
FJ	0.001458	1	0.000684	8.11E-05	0.002835	1.195671
GH	-0.004587	1	0.000659	-0.005914	-0.003261	1.110326
HJ	-0.004005	1	0.000656	-0.005325	-0.002685	1.216513
C^2	0.003753	1	0.00232	-0.000916	0.008422	1.319678
G^2	-0.005569	1	0.002431	-0.010463	-0.000675	1.449822

Final Equation in Terms of Coded Factors

1/Sqrt(Visc =		
0.033154		3.32E-02
0.004256	* A	4.26E-03
-0.003786	* B	-3.79E-03
-0.003393	* C	-3.39E-03
-0.003746	* D	-3.75E-03
0.002607	* E	2.61E-03
-0.000253	* F	-2.53E-04
0.000208	* G	2.08E-04
0.001331	* H	1.33E-03
0.001733	* J	1.73E-03
0.001278	* A * B	1.28E-03
0.001458	* A * C	1.46E-03
0.001413	* A * D	1.41E-03
-0.003308	* A * H	-3.31E-03
0.001931	* A * J	1.93E-03
-0.001349	* B * C	-1.35E-03
-0.001916	* B * H	-1.92E-03
0.001279	* C * E	1.28E-03
-0.001352	* D * E	-1.35E-03
0.003605	* D * H	3.61E-03
-0.001784	* E * F	-1.78E-03
-0.001347	* F * H	-1.35E-03
0.001458	* F * J	1.46E-03
-0.004587	* G * H	-4.59E-03
-0.004005	* H * J	-4.00E-03
0.003753	* C^2	3.75E-03
-0.005569	* G^2	-5.57E-03

Final Equation in Terms of Actual Factors

1/Sqrt(Visc =	
-0.046011	
-0.000729	* Mass Polyester
-5.08E-05	* Mass Styrene
-0.023624	* Mass LMA
-0.00395	* Mass DETA (Organic)
0.00025	* Mass Water
0.000366	* Stirrer Speed
0.006395	* Initial Temperature
0.007506	* Acid Value
-5.5E-05	* Viscosity
1.87E-06	* Mass Polyester * Mass Styrene
1.36E-05	* Mass Polyester * Mass LMA
4.23E-05	* Mass Polyester * Mass DETA (Organic
-7.25E-06	* Mass Polyester * Acid Value
2.5E-07	* Mass Polyester * Viscosity
-2.85E-05	* Mass Styrene * Mass LMA
-9.52E-06	* Mass Styrene * Acid Value
7.59E-06	* Mass LMA * Mass Water
-2.58E-05	* Mass DETA (Organic) * Mass Water
0.000366	* Mass DETA (Organic) * Acid Value
-5.78E-07	* Mass Water * Stirrer Speed
-2.32E-06	* Stirrer Speed * Acid Value
1.48E-07	* Stirrer Speed * Viscosity
-5.28E-05	* Initial Temperature * Acid Value
-1.76E-06	* Acid Value * Viscosity
0.000504	* Mass LMA^2
-9.9E-05	* Initial Temperature^2

Response **11 CR**

Backward Elimination Regression with Alpha to Exit = 0.100

Removed	**Coefficient Estimate**	**t for H0 Coeff=0**	**Prob > |t|**	**R-Squared**	**MSE**
AD	-0.01	-0.01	0.99	0.97	22.77
CE	-0.03	-0.05	0.96	0.97	22.04
BH	-0.03	-0.05	0.96	0.97	21.35
AE	-0.09	-0.13	0.90	0.97	20.72
EF	0.12	0.17	0.87	0.97	20.13
EG	0.15	0.23	0.82	0.97	19.58
BC	-0.18	-0.27	0.79	0.97	19.08
DE	0.18	0.27	0.79	0.97	18.60
CF	-0.27	-0.45	0.66	0.97	18.21
EH	0.29	0.47	0.64	0.97	17.85
AC	-0.34	-0.53	0.60	0.97	17.52
FJ	-0.33	-0.58	0.57	0.97	17.24
BF	-0.34	-0.59	0.56	0.97	16.97
B-Mass Styrene	0.35	0.66	0.51	0.97	16.75
CH	0.36	0.68	0.50	0.97	16.55
BE	-0.50	-0.89	0.38	0.97	16.47
AF	0.52	0.91	0.37	0.97	16.41
AJ	-0.50	-0.96	0.34	0.97	16.39
J-Viscosity	-0.50	-1.01	0.32	0.96	16.39
BJ	0.54	1.03	0.31	0.96	16.41
C-Mass LMA	0.52	0.98	0.33	0.96	16.40
CD	-0.50	-0.94	0.35	0.96	16.36
BD	0.62	1.16	0.25	0.96	16.47
FH	0.72	1.36	0.18	0.96	16.73
CJ	0.71	1.32	0.19	0.96	16.97
DF	0.75	1.42	0.16	0.96	17.28
GJ	0.72	1.40	0.17	0.96	17.57

Hierarchical Terms Added after Backward Elimination R egression
B-Mass Styrene, C-Mass LMA, J-Viscosity

ANOVA for Response Surface Reduced 2FI Model

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	21182.415	21	1008.6864	56.326969	**< 0.0001**	significant
A-Mass Polyester	51.484796	1	51.484796	2.8750089	**0.0958**	
B-Mass Styrene	16.966582	1	16.966582	0.9474462	0.3348	
C-Mass LMA	4.5085382	1	4.5085382	0.2517653	0.6179	
D-Mass DETA (Organic)	1610.2445	1	1610.2445	89.919116	**< 0.0001**	
E-Mass Water	232.02999	1	232.02999	12.956996	**0.0007**	
F-Stirrer Speed	865.43414	1	865.43414	48.327487	**< 0.0001**	
G-Initial Temperature	568.39503	1	568.39503	31.740259	**< 0.0001**	
H-Acid Value	13562.053	1	13562.053	757.33084	**< 0.0001**	
J-Viscosity	11.309632	1	11.309632	0.6315514	0.4303	
AB	136.15393	1	136.15393	7.6030944	**0.0080**	
AG	297.15251	1	297.15251	16.593561	**0.0002**	
AH	269.90603	1	269.90603	15.072066	**0.0003**	
BG	215.66913	1	215.66913	12.043374	**0.0010**	
CG	80.81877	1	80.81877	4.5130738	**0.0383**	
DG	77.054952	1	77.054952	4.302895	**0.0429**	
DH	511.00204	1	511.00204	28.535326	**< 0.0001**	
DJ	59.501836	1	59.501836	3.3226957	**0.0740**	
EJ	97.514089	1	97.514089	5.4453721	**0.0234**	
FG	77.540661	1	77.540661	4.3300179	**0.0423**	
GH	188.69082	1	188.69082	10.536854	**0.0020**	
HJ	997.96805	1	997.96805	55.728433	**< 0.0001**	
Residual	949.10809	53	17.9077			
Lack of Fit	851.68219	49	17.381269	0.7136201	0.7526	not significant
Pure Error	97.4259	4	24.356475			
Cor Total	22131.523	74				

Std. Dev.	4.232	**R-Squared**	0.957
Mean	69.375	**Adj R-Squar**	0.940
C.V. %	6.100	**Pred R-Squa**	0.913
PRESS	1916.369	**Adeq Precis**	26.687

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	69.255837	1	0.4964028	68.260179	70.251495	
A-Mass Polyester	-0.903233	1	0.532697	-1.971688	0.1652218	1.123167
B-Mass Styrene	0.5138903	1	0.5279504	-0.545044	1.5728247	1.0721106

C-Mass LMA	0.2720547	1	0.5421983	-0.815457	1.3595668	1.1128095
D-Mass DETA (Organic)	4.9985903	1	0.5271346	3.9412922	6.0558885	1.0687999
E-Mass Water	-2.066798	1	0.5741772	-3.218452	-0.915145	1.251875
F-Stirrer Speed	3.958052	1	0.5693566	2.8160672	5.1000368	1.2270811
G-Initial Temperature	-2.948772	1	0.5234027	-3.998585	-1.898959	1.0394418
H-Acid Value	-13.80681	1	0.5017075	-14.81311	-12.80051	1.0540117
J-Viscosity	-0.400347	1	0.5037697	-1.410781	0.6100873	1.0626944
AB	1.6089692	1	0.5835157	0.4385849	2.7793535	1.233605
AG	2.2741305	1	0.5582717	1.1543793	3.3938816	1.1138619
AH	-2.10116	1	0.5412186	-3.186707	-1.015613	1.161134
BG	1.9329003	1	0.5569746	0.8157508	3.0500499	1.1077681
CG	-1.173868	1	0.5525644	-2.282171	-0.065564	1.0739267
DG	-1.16087	1	0.559633	-2.283352	-0.038389	1.1183679
DH	2.9262679	1	0.5478008	1.8275186	4.0250171	1.1453095
DJ	0.9747213	1	0.5347308	-0.097813	2.0472554	1.0998253
EJ	-1.252976	1	0.5369438	-2.329948	-0.176003	1.091345
FG	1.2451054	1	0.5983582	0.0449508	2.44526	1.2593062
GH	1.7239804	1	0.5311007	0.6587274	2.7892334	1.0702421
HJ	3.8983725	1	0.5222097	2.8509525	4.9457925	1.1419158

Final Equation in Terms of Coded Factors:

CR	=	
69.255837		69.26
-0.903233	* A	-0.90
0.5138903	* B	0.51
0.2720547	* C	0.27
4.9985903	* D	5.00
-2.066798	* E	-2.07
3.958052	* F	3.96
-2.948772	* G	-2.95
-13.80681	* H	-13.81
-0.400347	* J	-0.40
1.6089692	* A * B	1.61
2.2741305	* A * G	2.27
-2.10116	* A * H	-2.10
1.9329003	* B * G	1.93
-1.173868	* C * G	-1.17
-1.16087	* D * G	-1.16
2.9262679	* D * H	2.93
0.9747213	* D * J	0.97
-1.252976	* E * J	-1.25
1.2451054	* F * G	1.25
1.7239804	* G * H	1.72
3.8983725	* H * J	3.90

Final Equation in Terms of Actual Factors:

CR	=
245.15326	
-0.302079	* Mass Polyester
-1.017937	* Mass Styrene
1.3904356	* Mass LMA
-12.91283	* Mass DETA (Organic)
0.1809991	* Mass Water
0.0044547	* Stirrer Speed
-4.767887	* Initial Temperature
-5.05762	* Acid Value
0.0174198	* Viscosity
0.0023572	* Mass Polyester * Mass Styrene
0.0077075	* Mass Polyester * Initial Temperature
-0.004606	* Mass Polyester * Acid Value
0.0148539	* Mass Styrene * Initial Temperature
-0.057365	* Mass LMA * Initial Temperature
-0.182256	* Mass DETA (Organic) * Initial Temperature
0.2971681	* Mass DETA (Organic) * Acid Value
0.0058409	* Mass DETA (Organic) * Viscosity
-0.000103	* Mass Water * Viscosity
0.0033203	* Stirrer Speed * Initial Temperature
0.0198244	* Initial Temperature * Acid Value
0.001711	* Acid Value * Viscosity

Response **16 Cost/kg**

Backward Elimination Regression with Alpha to Exit = 0.1 00

Removed	**Coefficient Estimate**	**t for H0 Coeff=0**	**Prob > |t|**	**R-Squared**	**MSE**
F-Stirrer Speed	-2.641E-04	-3.098E-01	7.577E-01	9.996E-01	4.711E-05
G-Initial Temperature	-3.980E-04	-4.767E-01	6.352E-01	9. 996E-01	4.657E-05
J-Viscosity	3.855E-04	4.868E-01	6.280E-01	9.996E-01	4.60 5E-05
H-Acid Value	1.017E-03	1.288E+00	2.020E-01	9.996E-01	4.64 9E-05

ANOVA for Response Surface Reduced Linear Model

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	7.49729	5	1.499458	32254.8	**< 0.0001**	significant
A-Mass Polyester	5.180885	1	5.180885	111445.9	**< 0.0001**	
B-Mass Styrene	0.168974	1	0.168974	3634.786	**< 0.0001**	
C-Mass LMA	0.792734	1	0.792734	17052.47	**< 0.0001**	
D-Mass DETA (Organic)	0.013735	1	0.013735	295.4424	**< 0.0001**	
E-Mass Water	1.821717	1	1.821717	39186.89	**< 0.0001**	
Residual	0.003208	69	4.65E-05			
Lack of Fit	0.003208	65	4.93E-05			
Pure Error	0	4	0			
Cor Total	7.500498	74				

Std. Dev.	0.007	**R-Squared**	1.000
Mean	5.347	**Adj R-Squar**	1.000
C.V. %	0.128	**Pred R-Squa**	0.999
PRESS	0.004	**Adeq Precis**	632.776

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	5.360668	1	0.000791	5.359091	5.362246	
A-Mass Polyester	0.272557	1	0.000816	0.270928	0.274186	1.016 327
B-Mass Styrene	0.049724	1	0.000825	0.048079	0.051369	1.00788
C-Mass LMA	0.1088	1	0.000833	0.107138	0.110462	1.012216
D-Mass DETA (Organic)	0.014162	1	0.000824	0.012518	0.015805	1.005806
E-Mass Water	-0.164905	1	0.000833	-0.166567	-0.163243	1.015068

Final Equation in Terms of Coded Factors:

Cost/kg	=	
5.360668		5.361
0.272557	* A	0.273
0.049724	* B	0.050
0.1088	* C	0.109
0.014162	* D	0.014
-0.164905	* E	-0.165

Final Equation in Terms of Actual Factors:

Cost/kg	=
5.06619	
0.006928	* Mass Polyester
0.002866	* Mass Styrene
0.039877	* Mass LMA
0.016675	* Mass DETA (Organic)
-0.002671	* Mass Water

Response **4 SMD**

Backward Elimination Regression with Alpha to Exit = 0.100

Removed	Coefficient Estimate	t for H0 Coeff=0	Prob > |t|	R-Squared	MSE
CE	0.00	0.01	0.99	0.94	7.00
EH	-0.08	-0.21	0.83	0.94	6.78
FG	-0.10	-0.26	0.80	0.94	6.58
AF	-0.15	-0.38	0.71	0.94	6.41
BE	0.16	0.45	0.66	0.94	6.26
CJ	-0.18	-0.50	0.62	0.94	6.13
DF	-0.17	-0.52	0.61	0.94	6.00
G-Initial Temperature	-0.21	-0.63	0.53	0.94	5.91
AH	0.22	0.65	0.52	0.94	5.82
BD	0.19	0.59	0.56	0.94	5.72
CD	0.30	0.87	0.39	0.93	5.68
EJ	0.27	0.84	0.40	0.93	5.64
CF	-0.41	-1.21	0.24	0.93	5.70
EF	-0.41	-1.22	0.23	0.93	5.77
DE	0.44	1.28	0.21	0.93	5.85
BC	-0.40	-1.18	0.24	0.92	5.90
GJ	-0.36	-1.15	0.26	0.92	5.94
DJ	0.49	1.52	0.14	0.92	6.11
CG	-0.49	-1.43	0.16	0.91	6.24
AJ	0.45	1.45	0.15	0.91	6.38
BH	-0.48	-1.47	0.15	0.91	6.53
BF	0.48	1.38	0.17	0.90	6.65
GH	-0.44	-1.36	0.18	0.90	6.76
AG	-0.51	-1.49	0.14	0.90	6.91

Hierarchical Terms Added after Backward Elimination R egression

G-Initial Temperature

ANOVA for Response Surface Reduced 2FI Model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	3128.0617	22	142.18462	20.18411	**< 0.0001**	significant
A-Mass Polyester	52.764883	1	52.764883	7.4903473	**0.0085**	
B-Mass Styrene	600.08703	1	600.08703	85.186587	**< 0.0001**	
C-Mass LMA	119.7594	1	119.7594	17.000692	**0.0001**	
D-Mass DETA (Organic)	31.422479	1	31.422479	4.4606425	**0.0395**	
E-Mass Water	171.3051	1	171.3051	24.317967	**< 0.0001**	
F-Stirrer Speed	506.68396	1	506.68396	71.927362	**< 0.0001**	
G-Initial Temperature	0.0697371	1	0.0697371	0.0098997	0.9211	
H-Acid Value	129.603	1	129.603	18.398059	**< 0.0001**	
J-Viscosity	559.76368	1	559.76368	79.462403	**< 0.0001**	
AB	65.937085	1	65.937085	9.3602342	**0.0035**	
AC	27.15999	1	27.15999	3.8555522	**0.0549**	
AD	23.652387	1	23.652387	3.3576232	**0.0726**	
AE	55.605965	1	55.605965	7.8936589	**0.0070**	
BG	127.23936	1	127.23936	18.062525	**< 0.0001**	
BJ	33.016501	1	33.016501	4.6869251	**0.0350**	
CH	112.79847	1	112.79847	16.012538	**0.0002**	
DG	36.207624	1	36.207624	5.1399276	**0.0276**	
DH	43.140248	1	43.140248	6.1240624	**0.0166**	
EG	31.590835	1	31.590835	4.4845418	**0.0390**	
FH	59.337365	1	59.337365	8.4233575	**0.0054**	
FJ	66.284111	1	66.284111	9.4094971	**0.0034**	
HJ	161.33574	1	161.33574	22.902747	**< 0.0001**	
Residual	366.30797	52	7.044384			
Lack of Fit	355.44607	48	7.4051265	2.7270096	0.1689	not significant
Pure Error	10.8619	4	2.715475			
Cor Total	3494.3697	74				

Std. Dev.	2.654	**R-Squared**	0.895
Mean	18.452	**Adj R-Squar**	0.851
C.V. %	14.384	**Pred R-Squa**	0.777
PRESS	778.445	**Adeq Precis**	18.387

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	18.305853	1	0.314027	17.675711	18.935994	
A-Mass Polyester	-0.924514	1	0.3378024	-1.602364	-0.246664	1.1481697
B-Mass Styrene	-3.176865	1	0.3442018	-3.867557	-2.486174	1.1584478
C-Mass LMA	1.4030729	1	0.3402882	0.7202346	2.0859111	1.1142819
D-Mass DETA (Organic)	0.6982119	1	0.3305891	0.0348363	1.3615875	1.0686296

E-Mass Water	1.6930599	1	0.3433276	1.0041227	2.3819971	1.1378455
F-Stirrer Speed	-3.129667	1	0.369021	-3.870162	-2.389173	1.3103988
G-Initial Temperature	-0.032761	1	0.3292675	-0.693485	0.6279624	1.0457379
H-Acid Value	-1.383994	1	0.3226622	-2.031463	-0.736525	1.1082485
J-Viscosity	2.8680698	1	0.3217428	2.2224456	3.5136939	1.101942
AB	-1.125204	1	0.3677797	-1.863208	-0.3872	1.2457857
AC	0.7382378	1	0.3759698	-0.016201	1.4926764	1.2799496
AD	0.6261626	1	0.3417206	-0.05955	1.3118752	1.071963
AE	-0.968388	1	0.3446752	-1.660029	-0.276746	1.0712419
BG	-1.493608	1	0.351437	-2.198818	-0.788398	1.1211659
BJ	-0.761149	1	0.3515811	-1.466648	-0.05565	1.2086518
CH	-1.358515	1	0.3394957	-2.039763	-0.677267	1.1117153
DG	0.8006111	1	0.3531369	0.0919901	1.5092321	1.1320382
DH	0.8572433	1	0.3464051	0.1621306	1.552356	1.164241
EG	-0.780587	1	0.3686061	-1.52025	-0.040925	1.2128147
FH	0.9972831	1	0.3436179	0.3077632	1.6868029	1.1361951
FJ	-1.058156	1	0.3449581	-1.750365	-0.365947	1.1486786
HJ	1.5410175	1	0.3220059	0.8948655	2.1871696	1.1037447

Final Equation in Terms of Coded Factors:

SMD	=	
18.305853		18.31
-0.924514	* A	-0.92
-3.176865	* B	-3.18
1.4030729	* C	1.40
0.6982119	* D	0.70
1.6930599	* E	1.69
-3.129667	* F	-3.13
-0.032761	* G	-0.03
-1.383994	* H	-1.38
2.8680698	* J	2.87
-1.125204	* A * B	-1.13
0.7382378	* A * C	0.74
0.6261626	* A * D	0.63
-0.968388	* A * E	-0.97
-1.493608	* B * G	-1.49
-0.761149	* B * J	-0.76
-1.358515	* C * H	-1.36
0.8006111	* D * G	0.80
0.8572433	* D * H	0.86
-0.780587	* E * G	-0.78
0.9972831	* F * H	1.00
-1.058156	* F * J	-1.06
1.5410175	* H * J	1.54

Final Equation in Terms of Actual Factors:

SMD	=
-249.3787	
0.4040245	* Mass Polyester
1.0376059	* Mass Styrene
-0.010657	* Mass LMA
-10.83286	* Mass DETA (Organic)
0.186021	* Mass Water
0.0986979	* Stirrer Speed
2.5241815	* Initial Temperature
-1.909721	* Acid Value
0.0536	* Viscosity
-0.001648	* Mass Polyester * Mass Styrene
0.0068777	* Mass Polyester * Mass LMA
0.0187414	* Mass Polyester * Mass DETA (Organic)
-0.000399	* Mass Polyester * Mass Water
-0.011478	* Mass Styrene * Initial Temperature
-0.000223	* Mass Styrene * Viscosity
-0.042942	* Mass LMA * Acid Value
0.1256953	* Mass DETA (Organic) * Initial Temperature
0.0870547	* Mass DETA (Organic) * Acid Value
-0.001686	* Mass Water * Initial Temperature
0.0017202	* Stirrer Speed * Acid Value
-0.000108	* Stirrer Speed * Viscosity
0.0006764	* Acid Value * Viscosity

Response **7 SDevV**
Transform: Natural log Constant: 0
Backward Elimination Regression with Alpha to Exit = 0.100

Removed	Coefficient Estimate	t for H0 Coeff=0	Prob > |t|	R-Squared	MSE
G-Initial Temperature	-0.002	-0.087	0.931	0.916	0.038
D-Mass DETA (Organic)	-0.003	-0.120	0.906	0.916	0.037
BE	0.003	0.116	0.908	0.916	0.036
CD	0.004	0.136	0.893	0.915	0.035
BF	0.005	0.185	0.855	0.915	0.034
BC	0.007	0.242	0.810	0.915	0.033
FG	-0.006	-0.217	0.830	0.915	0.032
CG	0.007	0.251	0.803	0.915	0.031
CJ	-0.010	-0.392	0.697	0.915	0.031
CE	0.011	0.442	0.661	0.914	0.030
FJ	-0.013	-0.552	0.584	0.914	0.029
DF	-0.015	-0.644	0.523	0.913	0.029
CF	0.015	0.619	0.540	0.912	0.029
AE	-0.021	-0.921	0.363	0.910	0.028
EJ	0.021	0.977	0.334	0.908	0.028
EG	-0.029	-1.203	0.236	0.905	0.029
GJ	-0.027	-1.213	0.231	0.902	0.029
EF	-0.024	-1.004	0.320	0.900	0.029
DE	0.026	1.105	0.275	0.897	0.029
EH	-0.033	-1.466	0.149	0.893	0.030
FH	0.032	1.406	0.166	0.888	0.030
AG	-0.036	-1.546	0.128	0.883	0.031

Hierarchical Terms Added after Backward Elimination Regression
D-Mass DETA (Organic), G-Initial Temperature

ANOVA for Response Surface Reduced 2FI Model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	12.00872	25	0.480349	14.79496	**< 0.0001**	significant
A-Mass Polyester	1.137346	1	1.137346	35.03077	**< 0.0001**	
B-Mass Styrene	0.279805	1	0.279805	8.618105	**0.0051**	
C-Mass LMA	1.103597	1	1.103597	33.9913	**< 0.0001**	
D-Mass DETA (Organic)	0.001722	1	0.001722	0.053046	0.8188	
E-Mass Water	1.300843	1	1.300843	40.06655	**< 0.0001**	
F-Stirrer Speed	1.199818	1	1.199818	36.95493	**< 0.0001**	
G-Initial Temperature	0.000738	1	0.000738	0.02272	0.8808	
H-Acid Value	1.063643	1	1.063643	32.76069	**< 0.0001**	
J-Viscosity	3.029607	1	3.029607	93.31325	**< 0.0001**	
AB	0.116111	1	0.116111	3.576286	**0.0645**	
AC	0.128438	1	0.128438	3.955945	**0.0523**	
AD	0.135019	1	0.135019	4.158652	**0.0468**	
AF	0.092474	1	0.092474	2.848253	0.0978	
AH	0.962338	1	0.962338	29.64043	**< 0.0001**	
AJ	0.108714	1	0.108714	3.348431	**0.0734**	
BD	0.170083	1	0.170083	5.238639	**0.0264**	
BG	0.108526	1	0.108526	3.342645	**0.0736**	
BH	0.269336	1	0.269336	8.29566	**0.0059**	
BJ	0.201648	1	0.201648	6.210838	**0.0161**	
CH	0.114141	1	0.114141	3.515587	**0.0668**	
DG	0.114913	1	0.114913	3.539368	**0.0659**	
DH	0.113395	1	0.113395	3.492608	**0.0676**	
DJ	0.189197	1	0.189197	5.827356	**0.0196**	
GH	0.121561	1	0.121561	3.74413	**0.0588**	
HJ	0.443904	1	0.443904	13.67246	**0.0005**	
Residual	1.590886	49	0.032467			
Lack of Fit	1.537285	45	0.034162	2.549367	0.1869	not significant
Pure Error	0.053601	4	0.0134			
Cor Total	13.59961	74				

Std. Dev.	0.180	**R-Squared**	0.883
Mean	3.042	**Adj R-Squa**	0.823
C.V. %	5.923	**Pred R-Squ**	0.727
PRESS	3.718	**Adeq Preci**	16.882

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	3.030264	1	0.021426	2.987207	3.07332	
A-Mass Polyester	-0.133348	1	0.02253	-0.178624	-0.088072	1.108162
B-Mass Styrene	-0.069264	1	0.023594	-0.116679	-0.02185	1.181024
C-Mass LMA	0.136845	1	0.023472	0.089677	0.184014	1.150252
D-Mass DETA (Organic)	-0.005172	1	0.022458	-0.050304	0.039959	1.070022
E-Mass Water	0.148981	1	0.023536	0.101683	0.196279	1.160233
F-Stirrer Speed	-0.148027	1	0.02435	-0.196961	-0.099094	1.23798

G-Initial Temperature	0.003483	1	0.023105	-0.042949	0.049914	1.117227
H-Acid Value	0.126611	1	0.022121	0.082158	0.171064	1.130143
J-Viscosity	0.2112	1	0.021864	0.167263	0.255137	1.104043
AB	-0.047862	1	0.025309	-0.098722	0.002998	1.280006
AC	0.051456	1	0.025871	-0.000533	0.103445	1.314932
AD	-0.048815	1	0.023938	-0.096919	-0.000711	1.141289
AF	-0.042492	1	0.025178	-0.093088	0.008105	1.240214
AH	0.126636	1	0.02326	0.079893	0.173379	1.182943
AJ	0.041107	1	0.022464	-0.004037	0.086251	1.101722
BD	0.054403	1	0.023769	0.006637	0.102169	1.130857
BG	-0.043752	1	0.02393	-0.091842	0.004338	1.127914
BH	-0.066306	1	0.023021	-0.112569	-0.020043	1.126113
BJ	0.059825	1	0.024005	0.011584	0.108065	1.222532
CH	-0.043331	1	0.02311	-0.089772	0.00311	1.117682
DG	0.045665	1	0.024273	-0.003113	0.094443	1.160427
DH	-0.044158	1	0.023628	-0.09164	0.003325	1.175262
DJ	0.056221	1	0.02329	0.009419	0.103024	1.150752
GH	-0.04436	1	0.022925	-0.09043	0.00171	1.099905
HJ	0.081743	1	0.022107	0.037317	0.126168	1.12874

Final Equation in Terms of Coded Factors:

Ln(SDevV)	=	
3.030264		3.030
-0.133348	* A	-0.133
-0.069264	* B	-0.069
0.136845	* C	0.137
-0.005172	* D	-0.005
0.148981	* E	0.149
-0.148027	* F	-0.148
0.003483	* G	0.003
0.126611	* H	0.127
0.2112	* J	0.211
-0.047862	* A * B	-0.048
0.051456	* A * C	0.051
-0.048815	* A * D	-0.049
-0.042492	* A * F	-0.042
0.126636	* A * H	0.127
0.041107	* A * J	0.041
0.054403	* B * D	0.054
-0.043752	* B * G	-0.044
-0.066306	* B * H	-0.066
0.059825	* B * J	0.060
-0.043331	* C * H	-0.043
0.045665	* D * G	0.046
-0.044158	* D * H	-0.044
0.056221	* D * J	0.056
-0.04436	* G * H	-0.044
0.081743	* H * J	0.082

Final Equation in Terms of Actual Factors:

Ln(SDevV)	=
9.863739	
-0.009158	* Mass Polyester
-0.015376	* Mass Styrene
-0.045272	* Mass LMA
-0.689346	* Mass DETA (Organic)
0.002413	* Mass Water
0.003577	* Stirrer Speed
0.0274	* Initial Temperature
-0.060264	* Acid Value
-0.005295	* Viscosity
-7.01E-05	* Mass Polyester * Mass Styrene
0.000479	* Mass Polyester * Mass LMA
-0.001461	* Mass Polyester * Mass DETA (Organic)
-2.16E-05	* Mass Polyester * Stirrer Speed
0.000278	* Mass Polyester * Acid Value
5.32E-06	* Mass Polyester * Viscosity
0.003692	* Mass Styrene * Mass DETA (Organic)
-0.000336	* Mass Styrene * Initial Temperature
-0.00033	* Mass Styrene * Acid Value
1.75E-05	* Mass Styrene * Viscosity
-0.00137	* Mass LMA * Acid Value
0.007169	* Mass DETA (Organic) * Initial Temperature
-0.004484	* Mass DETA (Organic) * Acid Value
0.000337	* Mass DETA (Organic) * Viscosity
-0.00051	* Initial Temperature * Acid Value
3.59E-05	* Acid Value * Viscosity

Response **6 SDevS**

Backward Elimination Regression with Alpha to Exit = 0.100

Removed	**Coefficient Estimate**	**t for H0 Coeff=0**	**Prob > |t|**	**R-Squared**	**MSE**
AD	0.01	0.04	0.97	0.96	6.32
BE	0.04	0.10	0.92	0.96	6.12
BJ	0.07	0.20	0.84	0.96	5.94
CE	0.09	0.25	0.80	0.96	5.77
CD	0.09	0.26	0.79	0.96	5.61
AF	-0.13	-0.36	0.72	0.96	5.47
FG	-0.13	-0.37	0.72	0.96	5.34
CJ	0.16	0.46	0.65	0.96	5.23
CF	-0.19	-0.57	0.57	0.95	5.13
CG	0.21	0.66	0.51	0.95	5.06
DH	-0.20	-0.64	0.53	0.95	4.99
EH	-0.27	-0.86	0.39	0.95	4.95
G-Initial Temperature	-0.27	-0.89	0.38	0.95	4.93
BF	0.36	1.17	0.25	0.95	4.97
DF	-0.33	-1.14	0.26	0.95	5.01
D-Mass DETA (Organic)	0.34	1.19	0.24	0.95	5.05
BC	-0.40	-1.26	0.21	0.95	5.12
AJ	0.40	1.43	0.16	0.94	5.23
FH	0.44	1.42	0.16	0.94	5.34
EF	-0.50	-1.59	0.12	0.94	5.51
GJ	-0.44	-1.44	0.16	0.93	5.63
DE	0.46	1.44	0.16	0.93	5.75

Hierarchical Terms Added after Backward Elimination Regression

D-Mass DETA (Organic), G-Initial Temperature

ANOVA for Response Surface Reduced 2FI Model

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	4042.441	25	161.6976	27.82477	**< 0.0001**	significant
A-Mass Polyester	141.6831	1	141.6831	24.38069	**< 0.0001**	
B-Mass Styrene	315.5678	1	315.5678	54.3026	**< 0.0001**	
C-Mass LMA	300.2345	1	300.2345	51.66407	**< 0.0001**	
D-Mass DETA (Organic)	7.864607	1	7.864607	1.353334	0.2503	
E-Mass Water	422.452	1	422.452	72.69513	**< 0.0001**	
F-Stirrer Speed	614.213	1	614.213	105.6932	**< 0.0001**	
G-Initial Temperature	0.517784	1	0.517784	0.0891	0.7666	
H-Acid Value	115.789	1	115.789	19.92486	**< 0.0001**	
J-Viscosity	986.6368	1	986.6368	169.7795	**< 0.0001**	
AB	58.9669	1	58.9669	10.14697	**0.0025**	
AC	26.51218	1	26.51218	4.562191	**0.0377**	
AE	29.18207	1	29.18207	5.021623	**0.0296**	
AG	46.05739	1	46.05739	7.925512	**0.0070**	
AH	152.4701	1	152.4701	26.2369	**< 0.0001**	
BD	40.39167	1	40.39167	6.95056	**0.0112**	
BG	127.1656	1	127.1656	21.88254	**< 0.0001**	
BH	85.38134	1	85.38134	14.69234	**0.0004**	
CH	70.37511	1	70.37511	12.11008	**0.0011**	
DG	32.28992	1	32.28992	5.556418	**0.0225**	
DJ	23.88408	1	23.88408	4.109949	**0.0481**	
EG	25.50852	1	25.50852	4.389481	**0.0414**	
EJ	29.79899	1	29.79899	5.127781	**0.0280**	
FJ	66.44854	1	66.44854	11.4344	**0.0014**	
GH	21.67003	1	21.67003	3.728958	**0.0593**	
HJ	367.9462	1	367.9462	63.31584	**< 0.0001**	
Residual	284.7529	49	5.811283			
Lack of Fit	265.9866	45	5.910814	1.259882	0.4645	not significant
Pure Error	18.76625	4	4.691563			
Cor Total	4327.194	74				

Std. Dev.	2.411	**R-Squared**	0.934
Mean	20.252	**Adj R-Squa**	0.901
C.V. %	11.903	**Pred R-Squ**	0.838
PRESS	703.149	**Adeq Preci**	21.146

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	20.138	1	0.283701	19.56788	20.70811	
A-Mass Polyester	-1.482747	1	0.300292	-2.086207	-0.879287	1.099866
B-Mass Styrene	-2.337116	1	0.317154	-2.974461	-1.699772	1.192233
C-Mass LMA	2.237879	1	0.311345	1.612207	2.863551	1.130725
D-Mass DETA (Organic)	0.353852	1	0.304172	-0.257405	0.965109	1.09663
E-Mass Water	2.618726	1	0.307141	2.001503	3.235948	1.103854
F-Stirrer Speed	-3.534604	1	0.343809	-4.225515	-2.843694	1.378818
G-Initial Temperature	-0.088981	1	0.2981	-0.688035	0.510072	1.039007

H-Acid Value	1.320769	1	0.295889	0.726158	1.915381	1.12972
J-Viscosity	3.816885	1	0.292932	3.228216	4.405553	1.107248
AB	-1.061694	1	0.333297	-1.731479	-0.391909	1.240228
AC	0.726041	1	0.339918	0.04295	1.409133	1.268256
AE	-0.708267	1	0.316064	-1.343422	-0.073113	1.091915
AG	-0.904912	1	0.321435	-1.550859	-0.258965	1.137872
AH	1.58623	1	0.309678	0.96391	2.208551	1.171453
BD	0.833259	1	0.316061	0.198112	1.468407	1.117102
BG	-1.482889	1	0.317	-2.119925	-0.845853	1.105772
BH	-1.172684	1	0.30594	-1.787493	-0.557876	1.111129
CH	-1.055608	1	0.303339	-1.665191	-0.446024	1.075856
DG	0.757783	1	0.321475	0.111754	1.403811	1.13721
DJ	0.632496	1	0.311989	0.00553	1.259461	1.153718
EG	-0.719284	1	0.343316	-1.409202	-0.029365	1.275345
EJ	0.705607	1	0.3116	0.079422	1.331791	1.132579
FJ	-1.055852	1	0.312245	-1.683332	-0.428371	1.140852
GH	-0.59126	1	0.306186	-1.206563	0.024043	1.09614
HJ	2.376354	1	0.298645	1.776205	2.976503	1.150859

Final Equation in Terms of Coded Factors:

SDevS	=	
20.138		20.14
-1.482747	* A	-1.48
-2.337116	* B	-2.34
2.237879	* C	2.24
0.353852	* D	0.35
2.618726	* E	2.62
-3.534604	* F	-3.53
-0.088981	* G	-0.09
1.320769	* H	1.32
3.816885	* J	3.82
-1.061694	* A * B	-1.06
0.726041	* A * C	0.73
-0.708267	* A * E	-0.71
-0.904912	* A * G	-0.90
1.58623	* A * H	1.59
0.833259	* B * D	0.83
-1.482889	* B * G	-1.48
-1.172684	* B * H	-1.17
-1.055608	* C * H	-1.06
0.757783	* D * G	0.76
0.632496	* D * J	0.63
-0.719284	* E * G	-0.72
0.705607	* E * J	0.71
-1.055852	* F * J	-1.06
-0.59126	* G * H	-0.59
2.376354	* H * J	2.38

Final Equation in Terms of Actual Factors:

SDevS	=
-43.87273	
0.292973	* Mass Polyester
0.563555	* Mass Styrene
-0.017341	* Mass LMA
-16.67145	* Mass DETA (Organic)
0.044842	* Mass Water
0.152461	* Stirrer Speed
3.574024	* Initial Temperature
-1.821755	* Acid Value
-0.056708	* Viscosity
-0.001555	* Mass Polyester * Mass Styrene
0.006764	* Mass Polyester * Mass LMA
-0.000292	* Mass Polyester * Mass Water
-0.003067	* Mass Polyester * Initial Temperature
0.003477	* Mass Polyester * Acid Value
0.05655	* Mass Styrene * Mass DETA (Organic)
-0.011396	* Mass Styrene * Initial Temperature
-0.005829	* Mass Styrene * Acid Value
-0.033368	* Mass LMA * Acid Value
0.118971	* Mass DETA (Organic) * Initial Temperature
0.00379	* Mass DETA (Organic) * Viscosity
-0.001553	* Mass Water * Initial Temperature
5.82E-05	* Mass Water * Viscosity
-0.000107	* Stirrer Speed * Viscosity
-0.006799	* Initial Temperature * Acid Value
0.001043	* Acid Value * Viscosity

Response **9 CV (VMD)**

Backward Elimination Regression with Alpha to Exit = 0100

Removed	Coefficient Estimate	t for H0 Coeff=0	Prob > |t|	R-Squared	MSE
G-Initial Temperature	0.58	0.80	0.43	0.40	35.03
J-Viscosity	0.57	0.83	0.41	0.39	34.88
D-Mass DETA (Organic)	0.69	0.96	0.34	0.38	34.83
C-Mass LMA	0.80	1.11	0.27	0.37	34.96
E-Mass Water	0.97	1.35	0.18	0.36	35.36
F-Stirrer Speed	1.08	1.48	0.14	0.34	35.95

ANOVA for Response Surface Reduced Linear Model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1290.1231	3	430.04102	11.96077	**< 0.0001**	significant
A-Mass Polyester	528.64647	1	528.64647	14.703292	**0.0003**	
B-Mass Styrene	323.05258	1	323.05258	8.9850904	**0.0037**	
H-Acid Value	426.83982	1	426.83982	11.871734	**0.0010**	
Residual	2552.7548	71	35.954293			
Lack of Fit	2510.0839	67	37.463939	3.5118937	0.1131	not significant
Pure Error	42.670925	4	10.667731			
Cor Total	3842.8779	74				

Std. Dev.	5.996	**R-Squared**	0.336
Mean	54.466	**Adj R-Squai**	0.308
C.V. %	11.009	**Pred R-Squa**	0.258
PRESS	2852.587	**Adeq Precis**	10.525

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	54.238197	1	0.6935941	52.85521	55.621184	
A-Mass Polyester	-2.733573	1	0.7128914	-4.155038	-1.312108	1.0018893
B-Mass Styrene	2.1677101	1	0.7231693	0.7257515	3.6096687	1.0018953
H-Acid Value	2.3863084	1	0.6925793	1.0053446	3.7672722	1.0003967

Final Equation in Terms of Coded Factors:

CV (VMD)	=	
54.238197		54.24
-2.733573	* A	-2.73
2.1677101	* B	2.17
2.3863084	* H	2.39

Final Equation in Terms of Actual Factors:

CV (VMD)	=
53.354882	
-0.069484	* Mass Polyester
0.124938	* Mass Styrene
0.2058049	* Acid Value

Response **8 CV (SMD)**

Backward Elimination Regression with Alpha to Exit = 0.100

Removed	**Coefficient Estimate**	**t for H0 Coeff=0**	**Prob > |t|**	**R-Squared**	**MSE**
DG	-0.06	-0.03	0.97	0.91	160.12
AJ	-0.09	-0.05	0.96	0.91	154.97
BF	0.16	0.08	0.93	0.91	150.16
EG	0.15	0.08	0.93	0.91	145.64
BH	-0.18	-0.11	0.91	0.91	141.41
CD	-0.28	-0.17	0.87	0.91	137.49
FG	0.30	0.17	0.87	0.91	133.78
DF	-0.35	-0.21	0.83	0.91	130.33
GH	0.31	0.21	0.84	0.91	127.05
CE	-0.35	-0.22	0.83	0.91	123.94
AB	0.44	0.27	0.79	0.91	121.07
GJ	-0.42	-0.28	0.78	0.91	118.35
AC	0.44	0.28	0.78	0.91	115.75
EJ	0.52	0.38	0.71	0.91	113.44
CJ	0.68	0.47	0.64	0.91	111.45
DE	0.71	0.47	0.64	0.91	109.53
EF	-0.69	-0.46	0.65	0.91	107.65
EH	-0.92	-0.67	0.51	0.90	106.38
AG	-0.97	-0.68	0.50	0.90	105.20
F-Stirrer Speed	-0.92	-0.67	0.51	0.90	104.02
A-Mass Polyester	-0.96	-0.72	0.48	0.90	103.00
AF	-1.07	-0.73	0.47	0.90	102.05
BC	1.15	0.85	0.40	0.90	101.49
FJ	1.06	0.81	0.42	0.90	100.84
BG	-1.38	-1.04	0.30	0.90	100.98
CH	1.45	1.14	0.26	0.89	101.53
AE	1.60	1.22	0.23	0.89	102.44
FH	-1.74	-1.36	0.18	0.89	103.95
HJ	1.66	1.37	0.18	0.88	105.51
G-Initial Temperature	1.98	1.54	0.13	0.88	107.96
BE	-2.13	-1.60	0.12	0.87	110.74
BD	2.11	1.57	0.12	0.87	113.38

Hierarchical Terms Added after Backward Elimination Regression

A-Mass Polyester, F-Stirrer Speed, G-Initial Temperature

ANOVA for Response Surface Reduced 2FI Model

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	45670.207	16	2854.3879	24.868806	**< 0.0001**	significant
A-Mass Polyester	32.689901	1	32.689901	0.2848102	0.5956	
B-Mass Styrene	3596.8315	1	3596.8315	31.337333	**< 0.0001**	
C-Mass LMA	2143.4878	1	2143.4878	18.6751	**< 0.0001**	
D-Mass DETA (Organic)	2033.2845	1	2033.2845	17.714956	**< 0.0001**	
E-Mass Water	1161.6617	1	1161.6617	10.120958	**0.0024**	
F-Stirrer Speed	79.730458	1	79.730458	0.6946502	0.4080	
G-Initial Temperature	158.57715	1	158.57715	1.3816007	0.2446	
H-Acid Value	22847.7	1	22847.7	199.0602	**< 0.0001**	
J-Viscosity	899.85707	1	899.85707	7.8399892	**0.0069**	
AD	2385.0135	1	2385.0135	20.779389	**< 0.0001**	
AH	6351.7184	1	6351.7184	55.339238	**< 0.0001**	
BJ	2489.8821	1	2489.8821	21.693055	**< 0.0001**	
CF	242.28431	1	242.28431	2.1108979	0.1516	
CG	602.72954	1	602.72954	5.2512708	**0.0256**	
DH	5856.2605	1	5856.2605	51.022569	**< 0.0001**	
DJ	437.76565	1	437.76565	3.8140257	**0.0557**	
Residual	6657.115	58	114.77785			
Lack of Fit	6554.3398	54	121.37666	4.7239679	0.0692	not significant
Pure Error	102.77518	4	25.693795			
Cor Total	52327.322	74				

Std. Dev.	10.713	**R-Squared**	0.873

Mean	112.388	**Adj R-Squa**	0.838
C.V. %	9.533	**Pred R-Squ**	0.784
PRESS	11283.057	**Adeq Preci**	21.877

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	112.66484	1	1.2564774	110.14973	115.17995	
A-Mass Polyester	-0.705752	1	1.3224359	-3.352895	1.9413905	1.0799779
B-Mass Styrene	7.4605666	1	1.3327258	4.7928261	10.128307	1.0659005
C-Mass LMA	5.7976109	1	1.3415832	3.1121405	8.4830814	1.062971
D-Mass DETA (Organic)	-5.557718	1	1.3204636	-8.200913	-2.914523	1.0463764
E-Mass Water	4.3493154	1	1.3671309	1.6127056	7.0859252	1.1073146
F-Stirrer Speed	-1.141107	1	1.3691254	-3.881709	1.5994954	1.1070639
G-Initial Temperature	1.5585247	1	1.3259356	-1.095624	4.2126732	1.0407704
H-Acid Value	17.82282	1	1.2632351	15.29418	20.351459	1.042544
J-Viscosity	3.5293993	1	1.2605006	1.0062332	6.0525655	1.0380353
AD	-6.302575	1	1.3826161	-9.070181	-3.534968	1.0770246
AH	10.058062	1	1.3520654	7.3516086	12.764515	1.1306134
BJ	6.3919749	1	1.372381	3.6448559	9.139094	1.1302759
CF	2.0751661	1	1.4282994	-0.783886	4.9342181	1.117617
CG	3.214847	1	1.4029045	0.4066286	6.0230653	1.0800572
DH	-9.690519	1	1.356644	-12.40614	-6.974901	1.0959508
DJ	2.6046072	1	1.3336763	-0.065036	5.2742503	1.0674214

Final Equation in Terms of Coded Factors

CV (SMD)	=	
112.66484		112.66
-0.705752	* A	-0.71
7.4605666	* B	7.46
5.7976109	* C	5.80
-5.557718	* D	-5.56
4.3493154	* E	4.35
-1.141107	* F	-1.14
1.5585247	* G	1.56
17.82282	* H	17.82
3.5293993	* J	3.53
-6.302575	* A * D	-6.30
10.058062	* A * H	10.06
6.3919749	* B * J	6.39
2.0751661	* C * F	2.08
3.214847	* C * G	3.21
-9.690519	* D * H	-9.69
2.6046072	* D * J	2.60

Final Equation in Terms of Actual Factors

CV (SMD)	=
461.74233	
-0.016104	* Mass Polyester
-3.463123	* Mass Styrene
-6.73403	* Mass LMA
53.801335	* Mass DETA (Organic)
0.0704517	* Mass Water
-0.230339	* Stirrer Speed
-1.935428	* Initial Temperature
-0.956817	* Acid Value
-0.265175	* Viscosity
-0.18864	* Mass Polyester * Mass DETA (Organic)
0.0220496	* Mass Polyester * Acid Value
0.0018748	* Mass Styrene * Viscosity
0.0152116	* Mass LMA * Stirrer Speed
0.1571056	* Mass LMA * Initial Temperature
-0.984091	* Mass DETA (Organic) * Acid Value
0.0156077	* Mass DETA (Organic) * Viscosity

Response **14 pH**

Backward Elimination Regression with Alpha to Exit = 0100

Removed	**Coefficient Estimate**	**t for H0 Coeff=0**	**Prob > |t|**	**R-Squared**	**MSE**
B-Mass Styrene	0.002	0.056	0.956	0.272	0.072
F-Stirrer Speed	-0.007	-0.203	0.840	0.271	0.071
E-Mass Water	-0.019	-0.581	0.563	0.268	0.071
D-Mass DETA (Organic)	0.028	0.865	0.390	0.260	0.071
J-Viscosity	-0.048	-1.555	0.125	0.234	0.072
A-Mass Polyester	-0.050	-1.559	0.124	0.207	0.073

ANOVA for Response Surface Reduced Linear Model

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	1.3612104	3	0.4537368	6.1833516	**0.0009**	significant
C-Mass LMA	0.2244316	1	0.2244316	3.0584686	0.0846	
G-Initial Temperature	0.5428107	1	0.5428107	7.3972164	**0.0082**	
H-Acid Value	0.6562985	1	0.6562985	8.9437844	**0.0038**	
Residual	5.2100083	71	0.0733804			
Lack of Fit	4.8698583	67	0.0726845	0.8547341	0.6680	not significant
Pure Error	0.34015	4	0.0850375			
Cor Total	6.5712187	74				

Std. Dev.	0.271	**R-Squared**	0.207
Mean	8.167	**Adj R-Squai**	0.174
C.V. %	3.317	**Pred R-Squ**	0.115
PRESS	5.813	**Adeq Precis**	7.693

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	8.1680294	1	0.0313427	8.1055338	8.2305251	
C-Mass LMA	-0.057567	1	0.0329171	-0.123202	0.0080678	1.0009408
G-Initial Temperature	0.0894247	1	0.0328794	0.0238651	0.1549843	1.0010016
H-Acid Value	-0.093627	1	0.0313069	-0.156051	-0.031203	1.0015748

Final Equation in Terms of Coded Factors:

pH	=	
8.1680294		8.17
-0.057567	* C	-0.06
0.0894247	* G	0.09
-0.093627	* H	-0.09

Final Equation in Terms of Actual Factors:

pH	=
8.4802603	
-0.021099	* Mass LMA
0.0119233	* Initial Temperature
-0.008075	* Acid Value

Appendix E.3 - Correlation Matrices

Correlations (Book2) Marked correlations are significant at p < .05000 N=44 (Casewise deletion of missing data)

	Means	Std.Dev.	A: Mass UPR	B: Mass Styrene	C: Mass LMA	D: Mass DETA	E: Mass Water	F: Stirrer Speed	G: Initial Reactor Temp.	H: UPR Acid Value	J: UPR Viscosity
A: Mass UPR	314.245	36.571	1	0.044	0.015	-0.026	-0.058	-0.08	-0.15	0.286	-0.045
B: Mass Styrene	116.063	16.937	0.044	1	0.187	-0.074	0.023	-0.127	0.001	-0.067	-0.116
C: Mass LMA	12.898	2.522	0.015	0.187	1	-0.052	-0.024	0	-0.034	-0.359	-0.077
D: Mass DETA	4.246	0.819	-0.026	-0.074	-0.052	1	0.155	-0.051	0.127	0	0.096
E: Mass Water	1034.525	57.756	-0.058	0.023	-0.024	0.155	1	0.106	0.081	-0.032	-0.09
F: Stirrer Speed	350	47.003	-0.08	-0.127	0	-0.051	0.106	1	-0.13	0	-0.049
G: Initial Reactor Temp.	22.33	7.141	-0.15	0.001	-0.034	0.127	0.081	-0.13	1	-0.078	0.022
H: UPR Acid Value	34.137	11.534	0.286	-0.067	-0.359	0	-0.032	0	-0.078	1	-0.017
J: UPR Viscosity	2058.636	197.949	-0.045	-0.116	-0.077	0.096	-0.09	-0.049	0.022	-0.017	1
AB	0.045	0.939	0.038	0.354	0.229	0.103	-0.005	0.105	-0.025	-0.041	-0.192
AC	-0.068	0.925	-0.274	0.208	0.331	0.026	0.142	-0.187	0.157	-0.191	0.068
AD	-0.023	0.927	0.035	0.103	0.02	0.39	0.083	0.027	0.052	-0.131	-0.027
AE	-0.023	0.902	0.202	0.001	0.132	0.08	0.416	-0.027	-0.001	-0.082	0.074
AG	-0.136	0.905	0.104	-0.023	0.121	0.053	0.015	-0.055	0.32	-0.028	-0.32
AH	0.205	0.954	-0.253	-0.055	-0.12	-0.126	-0.099	0.233	0.005	0.359	0.141
BD	-0.068	0.95	0.129	-0.023	0.164	0.025	0.138	0.078	-0.002	-0.186	-0.031
BG	0	0.94	-0.027	-0.051	-0.214	0	0.159	-0.105	0	-0.05	0.196
BH	-0.068	0.974	-0.029	-0.17	0.16	-0.173	-0.121	0.178	-0.052	0.011	-0.22
CH	-0.273	0.924	-0.094	0.187	-0.198	-0.052	-0.078	0	-0.086	-0.359	0.023
DG	0.114	0.92	0.014	-0.003	0.065	-0.079	0.123	0.027	0.03	-0.002	-0.114
DH	0	0.964	-0.13	-0.173	-0.052	-0.2	-0.103	0.051	-0.025	0	-0.096
DJ	0.091	0.96	-0.057	-0.027	0.029	-0.1	-0.165	-0.103	-0.125	-0.08	0.009
EG	0.068	0.9	-0.025	0.157	0.107	0.134	-0.09	-0.193	0.138	-0.116	-0.07
EJ	-0.091	0.936	0.112	0.079	0.078	-0.155	-0.15	0.053	-0.081	0.132	0.09
FJ	-0.045	0.939	0.202	0.179	-0.015	-0.103	0.058	-0.105	0.077	0.24	-0.004
GH	-0.068	0.95	0.023	-0.048	-0.101	-0.025	-0.124	0.026	-0.182	-0.038	-0.128
HJ	0	1.012	0.124	-0.212	0.05	-0.095	0.147	0.245	-0.121	-0.092	-0.183
Hold-up	0.249	0.018	0.852	0.353	0.159	-0.131	-0.396	-0.11	-0.195	0.203	-0.001
IFT	0.966	0.436	0.367	-0.197	-0.283	-0.236	0.195	-0.079	-0.119	0.487	0.155
μ_c	0.019	0.014	0.105	0.159	-0.125	-0.164	-0.276	-0.195	-0.16	-0.118	-0. 123
ρ_c	1003.032	1.138	0.211	0.186	-0.071	0.155	-0.151	-0.12	-0.034	0.313	-0.058
μ_d	0.208	0.126	0.321	-0.453	-0.199	0.363	0.046	-0.005	-0.164	0.084	0.471
ρ_d	1081.525	7.993	0.304	-0.722	-0.128	0.068	0.008	0.138	-0.031	0.553	0.221
VMD	40.118	16.218	-0.138	-0.355	0.136	0.081	0.25	-0.25	0.007	0.141	0.556

	AB	AC	AD	AE	AG	AH	BD	BG	BH	CH	DG	DH	DJ
A: Mass UPR	0.038	-0.274	0.035	0.202	0.104	-0.253	0.129	-0.027	-0.029	-0.094	0.014	-0.13	-0.057
B: Mass Styrene	0.354	0.208	0.103	0.001	-0.023	-0.055	-0.023	-0.051	-0.17	0.187	-0.003	-0.173	-0.027
C: Mass LMA	0.229	0.331	0.02	0.132	0.121	-0.12	0.164	-0.214	0.16	-0.198	0.065	-0.052	0.029
D: Mass DETA	0.103	0.026	0.39	0.08	0.053	-0.126	0.025	0	-0.173	-0.052	-0.079	-0.2	-0.1
E: Mass Water	-0.005	0.142	0.083	0.416	0.015	-0.099	0.138	0.159	-0.121	-0.078	0.123	-0.103	-0.165
F: Stirrer Speed	0.105	-0.187	0.027	-0.027	-0.055	0.233	0.078	-0.105	0.178	0	0.027	0.051	-0.103
G: Initial Reactor Temp.	-0.025	0.157	0.052	-0.001	0.32	0.005	-0.002	0	-0.052	-0.086	0.03	-0.025	-0.125
H: UPR Acid Value	-0.041	-0.191	-0.131	-0.082	-0.028	0.359	-0.186	-0.05	0.011	-0.359	-0.002	0	-0.08
J: UPR Viscosity	-0.192	0.068	-0.027	0.074	-0.32	0.141	-0.031	0.196	-0.22	0.023	-0.114	-0.096	0.009
AB	1	0.218	-0.052	0.001	-0.02	-0.166	-0.049	-0.184	0.156	0.122	0.128	-0.103	0.15
AC	0.218	1	-0.029	-0.086	-0.067	-0.274	-0.058	0.187	0.098	0.223	0.064	0.026	-0.124
AD	-0.052	-0.029	1	0.138	0.107	0.032	0.104	0.133	-0.105	0.02	-0.16	0.182	-0.024
AE	0.001	-0.086	0.138	1	-0.004	-0.076	-0.165	-0.027	-0.055	-0.147	0.339	-0.187	-0.024
AG	-0.02	-0.067	0.107	-0.004	1	-0.075	0.124	0.027	-0.09	-0.268	0.019	0	-0.093
AH	-0.166	-0.274	0.032	-0.076	-0.075	1	-0.087	-0.078	0.065	-0.014	-0.027	-0.025	-0.046
BD	-0.049	-0.058	0.104	-0.165	0.124	-0.087	1	0.104	-0.03	-0.048	0.009	-0.076	-0.121
BG	-0.184	0.187	0.133	-0.027	0.027	-0.078	0.104	1	-0.102	0.054	-0.108	0.051	-0.206
BH	0.156	0.098	-0.105	-0.055	-0.09	0.065	-0.03	-0.102	1	0.16	0.061	-0.074	-0.118
CH	0.122	0.223	0.02	-0.147	-0.268	-0.014	-0.048	0.054	0.16	1	-0.099	-0.052	-0.076
DG	0.128	0.064	-0.16	0.339	0.019	-0.027	0.009	-0.108	0.061	-0.099	1	-0.131	0.067
DH	-0.103	0.026	0.182	-0.187	0	-0.025	-0.076	0.051	-0.074	-0.052	-0.131	1	0.1
DJ	0.15	-0.124	-0.024	-0.024	-0.093	-0.046	-0.121	-0.206	-0.118	-0.076	0.067	0.1	1
EG	-0.031	0.118	0.336	-0.113	0.012	-0.125	0.169	0	-0.154	-0.005	0.075	-0.08	0.289
EJ	-0.154	0.073	-0.029	-0.03	-0.07	0.152	-0.033	-0.053	-0.084	0.132	0.309	0.206	0.165
FJ	0.002	-0.191	-0.028	0.136	0.047	0.088	-0.343	-0.053	-0.029	-0.015	0.033	-0.103	-0.047
GH	-0.075	-0.217	-0.002	-0.11	0.151	-0.138	0.046	-0.156	-0.005	-0.048	-0.018	0.127	0.236
HJ	0	-0.224	-0.025	0.127	0.051	-0.072	-0.121	0.049	-0.118	-0.05	0.225	0.095	0
Hold-up	0.149	-0.166	-0.001	0.038	0.035	-0.209	0.057	-0.109	-0.029	0.007	-0.072	-0.156	0.037
IFT	-0.193	-0.097	-0.268	0.287	-0.092	0.213	-0.016	-0.015	-0.1	-0.024	0.29	-0.342	-0.044
μ_c	0.132	-0.153	-0.157	-0.218	-0.16	-0.2	-0.157	-0.173	-0.122	0.218	0 .123	0.167	0.157
ρ_c	-0.082	0.046	0.32	-0.153	0.212	-0.045	0.034	-0.187	-0.302	-0.186	0.014	0.142	-0.043
μ_d	-0.386	-0.086	0.268	0.113	-0.049	0.011	-0.052	0.26	-0.152	-0.037	-0.104	0.013	0.046
ρ_d	-0.222	-0.172	-0.063	0.056	-0.004	0.133	0.072	-0.001	0.04	-0.452	0.05	0.185	-0.093
VMD	-0.281	0.106	-0.202	0.144	-0.165	0.246	0.075	0.029	-0.217	-0.295	0.156	-0.11	0.048

	EG	EJ	FJ	GH	HJ	Hold-up	IFT	μ_c	ρ_c	μ_d	ρ_d	VMD
A: Mass UPR	-0.025	0.112	0.202	0.023	0.124	0.852	0.367	0.105	0.211	0.321	0.304	-0.138
B: Mass Styrene	0.157	0.079	0.179	-0.048	-0.212	0.353	-0.197	0.159	0.186	-0.453	-0.722	-0.355
C: Mass LMA	0.107	0.078	-0.015	-0.101	0.05	0.159	-0.283	-0.125	-0.071	-0.199	-0.128	0.136
D: Mass DETA	0.134	-0.155	-0.103	-0.025	-0.095	-0.131	-0.236	-0.164	0.155	0.363	0.068	0.081
E: Mass Water	-0.09	-0.15	0.058	-0.124	0.147	-0.396	0.195	-0.276	-0.151	0.046	0.008	0.25
F: Stirrer Speed	-0.193	0.053	-0.105	0.026	0.245	-0.11	-0.079	-0.195	-0.12	-0.005	0.138	-0.25
G: Initial Reactor Temp.	0.138	-0.081	0.077	-0.182	-0.121	-0.195	-0.119	-0.16	-0.034	-0.164	-0.031	0.007
H: UPR Acid Value	-0.116	0.132	0.24	-0.038	-0.092	0.203	0.487	-0.118	0.313	0.084	0.553	0.141
J: UPR Viscosity	-0.07	0.09	-0.004	-0.128	-0.183	-0.001	0.155	-0.123	-0.058	0.471	0.221	0.556
AB	-0.031	-0.154	0.002	-0.075	0	0.149	-0.193	0.132	-0.082	-0.386	-0.222	-0.281
AC	0.118	0.073	-0.191	-0.217	-0.224	-0.166	-0.097	-0.153	0.046	-0.086	-0.172	0.106
AD	0.336	-0.029	-0.028	-0.002	-0.025	-0.001	-0.268	-0.157	0.32	0.268	-0.063	-0.202
AE	-0.113	-0.03	0.136	-0.11	0.127	0.038	0.287	-0.218	-0.153	0.113	0.056	0.144
AG	0.012	-0.07	0.047	0.151	0.051	0.035	-0.092	-0.16	0.212	-0.049	-0.004	-0.165
AH	-0.125	0.152	0.088	-0.138	-0.072	-0.209	0.213	-0.2	-0.045	0.011	0.133	0.246
BD	0.169	-0.033	-0.343	0.046	-0.121	0.057	-0.016	-0.157	0.034	-0.052	0.072	0.075
BG	0	-0.053	-0.053	-0.156	0.049	-0.109	-0.015	-0.173	-0.187	0.26	-0.001	0.029
BH	-0.154	-0.084	-0.029	-0.005	-0.118	-0.029	-0.1	-0.122	-0.302	-0.152	0.04	-0.217
CH	-0.005	0.132	-0.015	-0.048	-0.05	0.007	-0.024	0.218	-0.186	-0.037	-0.452	-0.295
DG	0.075	0.309	0.033	-0.018	0.225	-0.072	0.29	0.123	0.014	-0.104	0.05	0.156
DH	-0.08	0.206	-0.103	0.127	0.095	-0.156	-0.342	0.167	0.142	0.013	0.185	-0.11
DJ	0.289	0.165	-0.047	0.236	0	0.037	-0.044	0.157	-0.043	0.046	-0.093	0.048
EG	1	0.09	0.031	-0.076	0.026	0.107	-0.051	0.178	0.214	0.151	-0.219	-0.015
EJ	0.09	1	0.101	0.019	-0.049	0.151	0.196	0.176	0.112	0.076	0.067	0.133
FJ	0.031	0.101	1	0.023	0	0.169	0.235	0.172	0.056	-0.026	0.007	-0.102
GH	-0.076	0.019	0.023	1	0.024	0.004	-0.165	0.195	0.028	-0.041	-0.075	-0.218
HJ	0.026	-0.049	0	0.024	1	0	0.099	0.108	-0.125	0.157	0.049	0.158
Hold-up	0.107	0.151	0.169	0.004	0	1	0.16	0.226	0.253	0.118	0.021	-0.276
IFT	-0.051	0.196	0.235	-0.165	0.099	0.16	1	-0.01	0.157	0.227	0.404	0.352
μ_c	0.178	0.176	0.172	0.195	0.108	0.226	-0.01	1	0. 215	-0.116	-0.23	-0.199
ρ_c	0.214	0.112	0.056	0.028	-0.125	0.253	0.157	0.215	1	0.067	0.082	-0.083
μ_d	0.151	0.076	-0.026	-0.041	0.157	0.118	0.227	-0.116	0.067	1	0.436	0.382
ρ_d	-0.219	0.067	0.007	-0.075	0.049	0.021	0.404	-0.23	0.082	0.436	1	0.413
VMD	-0.015	0.133	-0.102	-0.218	0.158	-0.276	0.352	-0.199	-0.083	0.382	0.413	1

Correlations (correlations.sta) Marked correlations are significant at $p < .05000$ N=44 (Casewise deletion of missing data)

	Means	Std.Dev.	A: Mass UPR	B: Mass Styrene	C: Mass LMA	D: Mass DETA	E: Mass Water	F: Stirrer Speed	G: Initial Reactor Temp.	H: UPR Acid Value	J: UPR Viscosity
Mass Polyester /g	314.245	36.5714	1	0.043682	0.014765	-0.025938	-0.058342	-0 .079836	-0.149893	0.285797	-0.045152
Mass Styrene /g	116.063	16.9373	0.043682	1	0.18747	-0.0741	0.023149	-0.126 709	0.000569	-0.067495	-0.116093
Mass LMA /g	12.898	2.5215	0.014765	0.18747	1	-0.05218	-0.024452	0	-0.03 3638	-0.358766	-0.077209
Mass DETA (Organic) /g	4.246	0.8191	-0.025938	-0.0741	-0.05218	1	0.154638	-0.0512 99	0.126629	0	0.095743
Mass Water /g	1034.525	57.7563	-0.058342	0.023149	-0.024452	0.154638	1	0 .10577	0.080701	-0.031806	-0.08973
Stirrer Speed /g	350	47.0032	-0.079836	-0.126709	0	-0.051299	0.10577	1	-0.12 9919	0	-0.049115
Initial Temperature /°C	22.33	7.1406	-0.149893	0.000569	-0.033638	0.126629	0.0807 01	-0.129919	1	-0.078135	0.022043
AV - Polyester /gKOH	34.137	11.5336	0.285797	-0.067495	-0.358766	0	-0.031806	0	-0.078135	1	-0.016879
Visc - Polyester /cP	2058.636	197.9487	-0.045152	-0.116093	-0.077209	0.095743	-0.08973	-0.049115	0.022043	-0.016879	1
AE	-0.023	0.9019	0.202361	0.0006	0.131893	0.080204	0.415928	-0.027429	-0.000616	-0.082481	0.074463
BE	0.023	0.9273	-0.007971	0.127865	-0.019735	0.130009	0.0243 69	0.133386	0.158643	-0.121476	0.076948
BG	0	0.9401	-0.026612	-0.050684	-0.214143	0	0.158656	-0.10526 3	0	-0.049741	0.19646
BH	-0.068	0.974	-0.028603	-0.169539	0.159704	-0.173285	-0.12 0643	0.177787	-0.051865	0.010911	-0.219775
CD	-0.045	0.9389	0.042388	0.178758	0.038982	-0.256802	-0.101 084	0.052695	0.024832	-0.058855	-0.00447
CH	-0.273	0.9242	-0.093511	0.18747	-0.19802	-0.05218	-0.0782 45	0	-0.086499	-0.358766	0.022709
DE	0.136	0.9045	0.033943	0.128094	-0.065755	0.106628	-0.0699 52	-0.164097	0.138705	-0.075192	-0.139212
DH	0	0.9645	-0.12969	-0.172901	-0.05218	-0.2	-0.103092	0.0512 99	-0.025326	0	-0.095743
EG	0.068	0.8996	-0.02465	0.157092	0.106807	0.134023	-0.09043 7	-0.192506	0.137621	-0.115775	-0.069991
EH	-0.045	0.9389	-0.064187	-0.125707	-0.121818	-0.102721	-0. 101084	-0.158084	-0.131257	0.090546	0.143051
EJ	-0.091	0.9356	0.111822	0.078707	0.078245	-0.154638	-0.149 758	0.052885	-0.080701	0.131766	0.08973
FJ	-0.045	0.9389	0.20225	0.178758	-0.014618	-0.102721	0.0577 62	-0.105389	0.076862	0.239947	-0.00447
GH	-0.068	0.9499	0.023345	-0.048451	-0.101151	-0.025385	-0.1 23713	0.026045	-0.181766	-0.03804	-0.128151
GJ	0.023	0.9521	-0.323077	0.199608	-0.019222	-0.126629	-0.080701	0.077951	-0.07638 5	-0.118318	-0.022043
Theoretical Holdup	0.249	0.0182	0.851693	0.352746	0.158918	-0.131054	-0.396175	-0.109687	-0.194665	0.203276	-0.000787
IFT /mN.m-1	0.966	0.4364	0.366699	-0.197398	-0.283252	-0.235952	0.19524	-0.078804	-0.11891 6	0.48733	0.155157
Viscosity /Pa.s	0.019	0.0139	0.105443	0.158836	-0.125324	-0.163925	-0.276 112	-0.195293	-0.160395	-0.117742	-0.123372
Density /kg.m-3	1003.032	1.1383	0.210685	0.185599	-0.071142	0.154634	-0.1 51276	-0.119532	-0.033651	0.313318	-0.058262
Viscosity /Pa.s	0.208	0.1257	0.321006	-0.45262	-0.19919	0.362943	0.046101	-0.005	-0.164426	0.083714	0.471094
Density /kg.m-3	1081.525	7.993	0.304455	-0.721942	-0.128131	0.067875	0.008397	0.138038	-0.030789	0.552535	0.22066
Buildup	0.932	1.3537	0.256629	0.441165	0.17068	0.071249	-0.068444	0.25585	-0.073408	0.180563	-0.328676

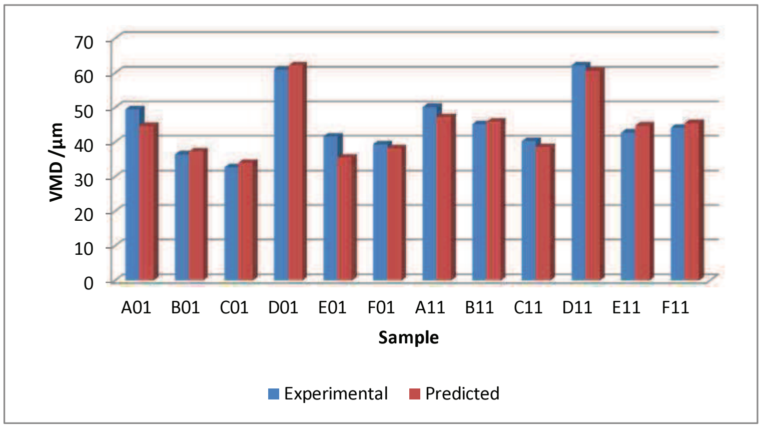
	AE	BE	BG	BH	CD	CH	DE	DH	EG	EH	EJ
Mass Polyester /g	0.202361	-0.007971	- 0.026612	-0.028603	0.042388	-0.093511	0.033943	-0.12969	- 0.02465	-0.064187	0.111822
Mass Styrene /g	0.0006	0.127865	-0.05068 4	-0.169539	0.178758	0.18747	0.128094	-0.172901	0.157092	- 0.125707	0.078707
Mass LMA /g	0.131893	-0.019735	-0.214143	0.159704	0.038982	-0.19802	-0.065755	-0.05218	0.106807	-0.121818	0.078245
Mass DETA (Organic) /g	0.080204	0.130009	0	-0.173285	-0.256 802	-0.05218	0.106628	-0.2	0.134023	-0.102721	-0.154638
Mass Water /g	0.415928	0.024369	0.158656	-0.120643	-0.101084	-0.078245	-0.06995 2	-0.103092	-0.090437	-0.101084	-0.149758
Stirrer Speed /g	-0.027429	0.133386	-0.105263	0.177787	0.0 52695	0	-0.164097	0.051299	-0.192506	-0.158084	0.052885
Initial Temperature /°C	-0.000616	0.158643	0	-0.0 51865	0.024832	-0.086499	0.138705	-0.025326	0.137621	-0.1 31257	-0.080701
AV - Polyester /gKOH	-0.082481	-0.121476	-0. 049741	0.010911	-0.058855	-0.358766	-0.075192	0	-0.115775	0.090546	0.131766
Visc - Polyester /cP	0.074463	0.076948	0.19646	-0.219775	-0.00447	0.022709	-0.139212	-0.095743	- 0.069991	0.143051	0.08973
AE	1	-0.05498	-0.0274 29	-0.054751	-0.083635	-0.147112	0.032394	-0.187144	-0.11 2704	0.245912	-0.030067
BE	-0.05498	1	0.10670 9	-0.023992	-0.025495	0.034536	-0.031506	-0.130009	0.0538 56	-0.025495	-0.131592
BG	-0.027429	0.106709	1	-0.101593	-0.105 389	0.053536	0.164097	0.051299	0	-0.158084	-0.052885
BH	-0.054751	-0.0 23992	-0.101593	1	-0.028896	0.159704	-0.121181	-0.074265	- 0.153823	0.021961	-0.083522
CD	-0.083635	-0.025 495	-0.105389	-0.028896	1	-0.068218	-0.047297	-0.256802	0. 031288	-0.055156	-0.163659
CH	-0.147112	0.034536	0.053536	0.159704	-0.068218	1	-0.010116	-0.05218	-0.005086	-0.068218	0.132039
DE	0.032394	-0.031 506	0.164097	-0.121181	-0.047297	-0.010116	1	-0.053314	0.1 31213	0.007468	0.069952
DH	-0.187144	-0.130009	0.051299	-0.0 74265	-0.256802	-0.05218	-0.053314	1	-0.080414	0.154081	0. 206185
EG	-0.112704	0.0538 56	0	-0.153823	0.031288	-0.005086	0.131213	-0.080414	1	-0.0 78847	0.090437
EH	0.245912	-0. 025495	-0.158084	0.021961	-0.055156	-0.068218	0.007468	0. 154081	-0.078847	1	-0.004814
EJ	-0.030067	-0.1315 92	-0.052885	-0.083522	-0.163659	0.132039	0.069952	0.2061 85	0.090437	-0.004814	1
FJ	0.136063	-0.18575	-0.052695	-0.028896	-0.055156	-0.014618	-0.21159	-0.1027 21	0.031288	0.103118	0.101084
GH	-0.110438	-0. 156614	-0.156268	-0.005142	-0.133935	-0.048167	-0.07013	0 .126926	-0.076085	0.074672	0.019033
GJ	-0.053551	-0.05328	-0.103935	0.0518 65	0.235317	0.139359	0.293366	0.227933	-0.137621	0.027197	0.080701
Theoretical Holdup	0.038248	0.018585	-0.109219	-0.02921	0.164103	0.007007	0.128179	-0.155819	0 .107022	-0.035845	0.150597
IFT /mN.m-1	0.286934	-0.014695	-0.015307	-0.100293	0.108492	-0.023748	-0.131044	-0.342047	-0.05137	0.279344	0.195551
Viscosity /Pa.s	-0.217651	-0. 156786	-0.172999	-0.121602	0.171843	0.217548	0.151233	0.1 67054	0.178265	0.192199	0.176114
Density /kg.m-3	-0.153317	0.096238	-0.186904	-0.302138	0.292956	-0.186096	0.058931	0.141924	0.213594	0.105828	0. 111968
Viscosity /Pa.s	0.11341	-0.056365	0.260078	-0.152123	-0.283042	-0.037255	0.016843	0.012854	0.151244	0.052648	0.07601
Density /kg.m-3	0.05589	-0.142208	-0.000619	0.040251	-0.119456	-0.452394	-0.229504	0.184921	-0.218888	0.047256	0.067486
Buildup	-0.001299	-0.035789	0	0.119857	0.198771	-0.126743	0.14072	0.106874	-0.053388	-0.258652	-0.041734

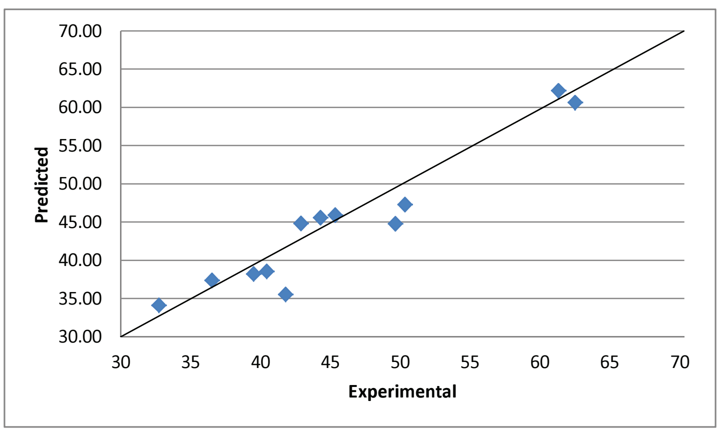
	FJ	GH	GJ	Hold-up	IFT	μ_c	ρc	μd	ρd	Buildup
Mass Polyester /g	0.20225	0.023345	-0.323077	0.851693	0.366699	0.105443	0.210685	0.321006	0.304455	0.256629
Mass Styrene /g	0.178758	-0.048451	0.199608	0.352746	-0.197398	0.158836	0.185599	-0.45262	-0.721942	0.441165
Mass LMA /g	- 0.014618	-0.101151	-0.019222	0.158918	-0.283252	-0.12532 4	-0.071142	-0.19919	-0.128131	0.17068
Mass DETA (Organic) /g	-0 .102721	-0.025385	-0.126629	-0.131054	-0.235952	-0.16392 5	0.154634	0.362943	0.067875	0.071249
Mass Water /g	0.057762	-0.123 713	-0.080701	-0.396175	0.19524	-0.276112	-0.151276	0.046101	0.008397	-0.068444
Stirrer Speed /g	-0 .105389	0.026045	0.077951	-0.109687	-0.078804	-0.195293	- 0.119532	-0.005	0.138038	0.25585
Initial Temperature /°C	0.076862	-0.181766	-0.076385	-0.194665	-0 .118916	-0.160395	-0.033651	-0.164426	-0.030789	-0.07340 8
AV - Polyester /gKOH	0.239947	-0.03804	-0.118318	0.203276	0.48733	-0.117742	0.313318	0.083714	0.552535	0.180563
Visc - Polyester /cP	-0.00447	-0.128151	-0.022043	-0 .000787	0.155157	-0.123372	-0.058262	0.471094	0.22066	-0.328676
AE	0.136063	-0.110438	-0.053551	0.03 8248	0.286934	-0.217651	-0.153317	0.11341	0.05589	-0.0012 99
BE	-0.18575	-0.156614	-0.05328	0.0185 85	-0.014695	-0.156786	0.096238	-0.056365	-0.142208	-0.03 5789
BG	-0.05 2695	-0.156268	-0.103935	-0.109219	-0.015307	-0.172999	-0 .186904	0.260078	-0.000619	0
BH	-0.028896	-0.005142	0.051865	-0.02921	-0.100293	-0.121602	-0.302138	-0.152123	0.040251	0.119857
CD	-0.055156	-0.133935	0.235317	0 .164103	0.108492	0.171843	0.292956	-0.283042	-0.119456	0. 198771
CH	-0.01461 8	-0.048167	0.139359	0.007007	-0.023748	0.217548	-0.18609 6	-0.037255	-0.452394	-0.126743
DE	-0.21159	-0.07013	0.293366	0.1281 79	-0.131044	0.151233	0.058931	0.016843	-0.229504	0.14072
DH	-0.102721	0.126926	0.227933	-0.155819	-0.342047	0.167054	0.141924	0.012854	0.184921	0.106874
EG	0.031288	-0.076085	-0.137621	0.107022	-0.0 5137	0.178265	0.213594	0.151244	-0.218888	-0.053388
EH	0.103118	0.074672	0.027197	-0 .035845	0.279344	0.192199	0.105828	0.052648	0.047256	-0.2 58652
EJ	0.101084	0.019033	0.080701	0.15059 7	0.195551	0.176114	0.111968	0.07601	0.067486	-0.041734
FJ	1	0.02252	-0.128892	0.169352	0.23507	0.172378	0.055782	-0.025589	0.006972	-0.222058
GH	0.02252	1	0.078901	0.0 04462	-0.164566	0.194789	0.027864	-0.040728	-0.074817	0.1 40994
GJ	-0.128892	0.078901	1	-0.144558	-0.261736	0.15159	-0.013558	-0.316439	-0.272974	0.181675
Theoretical Holdup	0.169352	0.004462	-0.144558	1	0 .160497	0.226199	0.252884	0.11849	0.02057	0.397568
IFT /mN.m-1	0.23507	-0.164566	-0.261736	0. 160497	1	-0.009834	0.157273	0.227406	0.403751	-0.322957
Viscosity /Pa.s	0.172378	0.194789	0.1515 9	0.226199	-0.009834	1	0.215464	-0.115598	-0.230402	0.0027 92
Density /kg.m-3	0.055782	0.027864	-0.013558	0.252884	0.157273	0.21 5464	1	0.067366	0.081806	0.190097
Viscosity /Pa.s	-0.025589	-0. 040728	-0.316439	0.11849	0.227406	-0.115598	0.067366	1	0.435724	-0.264426
Density /kg.m-3	0.006972	- 0.074817	-0.272974	0.02057	0.403751	-0.230402	0.081806	0.435724	1	-0.146209
Buildup	-0.222058	0.14099 4	0.181675	0.397568	-0.322957	0.002792	0.190097	-0.264426	-0.146209	1

Appendix E.4 - Model Prediction Results

VMD	Experimental	Predicted	95% CI Low	95% CI High	95% PI Low	95% PI High	PoE(VMD)	%error
SCR - A01	49.51	44.79	42.42	47.16	34.69	54.88	6.82	10.54%
SCR - B01	36.48	37.40	34.74	40.06	27.23	47.56	5.32	2.46%
SCR - C01	32.72	34.10	31.72	36.48	24.01	44.20	8.62	4.06%
SCR - D01	61.07	62.19	59.64	64.73	52.05	72.32	9.62	1.80%
SCR - E01	41.71	35.53	32.58	38.48	25.28	45.78	5.67	17.39%
SCR - F01	39.45	38.22	36.10	40.34	28.18	48.26	5.46	3.22%
SCR - A11	50.18	47.29	41.83	52.74	36.06	58.51	6.04	6.12%
SCR - B11	45.22	45.92	40.84	50.99	34.87	56.96	5.36	1.52%
SCR - C11	40.36	38.57	33.54	43.60	27.54	49.59	7.59	4.64%
SCR - D11	62.27	60.63	55.73	65.54	49.66	71.60	8.08	2.70%
SCR - E11	42.81	44.83	39.65	50.01	33.73	55.92	5.76	4.50%
SCR - F11	44.19	45.57	41.06	50.08	34.77	56.37	5.21	3.03%

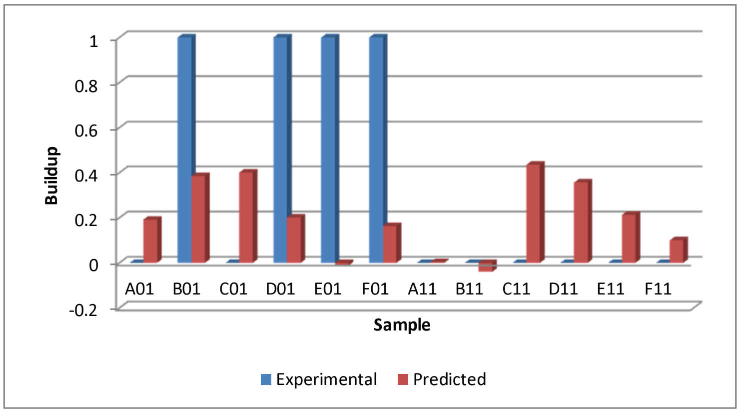
average error	5.16%

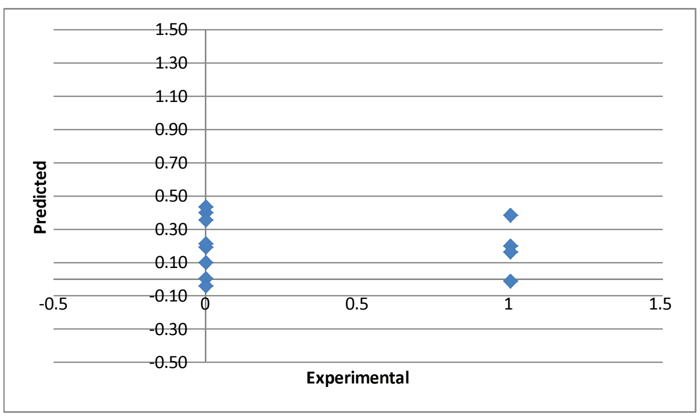




Buildup	Experimental	Predicted	95% CI Low	95% CI High	95% PI Low	95% PI High	PoE(Buildup)	%error
SCR - A01	0	0.19	0.11	0.31	-0.01	1.57	0.21	100.00%
SCR - B01	1	0.38	0.23	0.62	0.01	2.89	0.38	159.79%
SCR - C01	0	0.40	0.25	0.62	0.02	2.97	0.39	100.00%
SCR - D01	1	0.20	0.12	0.33	-0.01	1.64	0.19	398.64%
SCR - E01	1	-0.01	-0.04	0.05	-0.05	0.26	0.02	-8683.80%
SCR - F01	1	0.16	0.04	0.47	-0.02	1.64	0.19	511.79%
SCR - A11	0	0.00	-0.03	0.09	-0.04	0.38	0.00	100.00%
SCR - B11	0	-0.04	-0.05	-0.03	-0.05	0.03	0.04	-100.00%
SCR - C11	0	0.43	0.25	0.73	0.02	3.26	0.42	100.00%
SCR - D11	0	0.36	0.23	0.54	0.01	2.66	0.35	100.00%
SCR - E11	0	0.21	0.05	0.61	-0.02	2.04	0.24	100.00%
SCR - F11	0	0.10	0.02	0.29	-0.03	1.09	0.12	100.00%

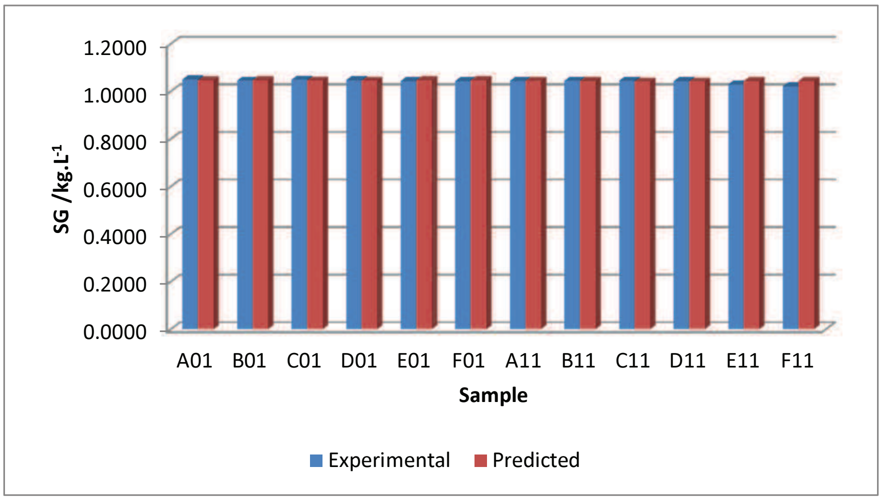
average error	-584.46%

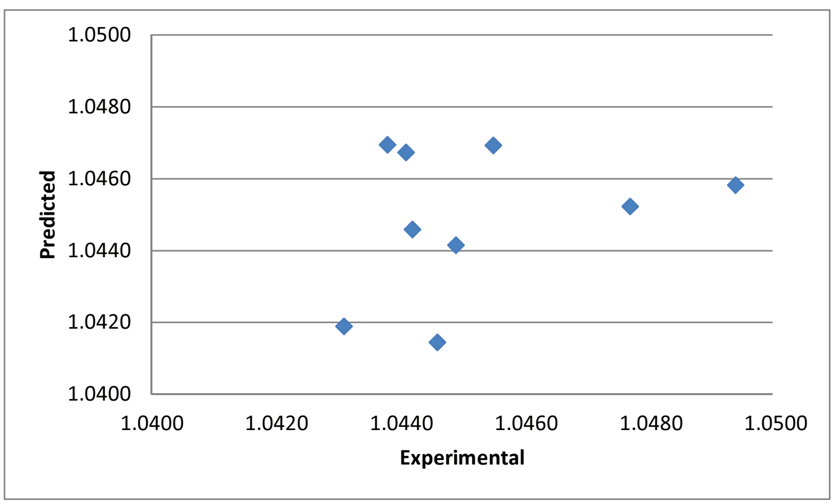




SG	Experimental	Predicted	95% CI Low	95% CI High	95% PI Low	95% PI High	%error
SCR - A01	1.0509	1.0463	1.0446	1.0480	1.0381	1.0546	0.44%
SCR - B01	1.0455	1.0469	1.0452	1.0487	1.0387	1.0552	0.14%
SCR - C01	1.0494	1.0458	1.0441	1.0475	1.0376	1.0541	0.34%
SCR - D01	1.0477	1.0452	1.0435	1.0469	1.0370	1.0535	0.24%
SCR - E01	1.0438	1.0469	1.0450	1.0489	1.0387	1.0552	0.30%
SCR - F01	1.0441	1.0467	1.0452	1.0483	1.0385	1.0549	0.25%
SCR - A11	1.0442	1.0446	1.0413	1.0478	1.0359	1.0533	0.04%
SCR - B11	1.0449	1.0441	1.0409	1.0474	1.0355	1.0528	0.07%
SCR - C11	1.0446	1.0414	1.0382	1.0447	1.0328	1.0501	0.30%
SCR - D11	1.0431	1.0419	1.0386	1.0452	1.0332	1.0506	0.12%
SCR - E11	1.0295	1.0439	1.0406	1.0472	1.0352	1.0526	1.38%
SCR - F11	1.0219	1.0439	1.0409	1.0469	1.0353	1.0525	2.11%

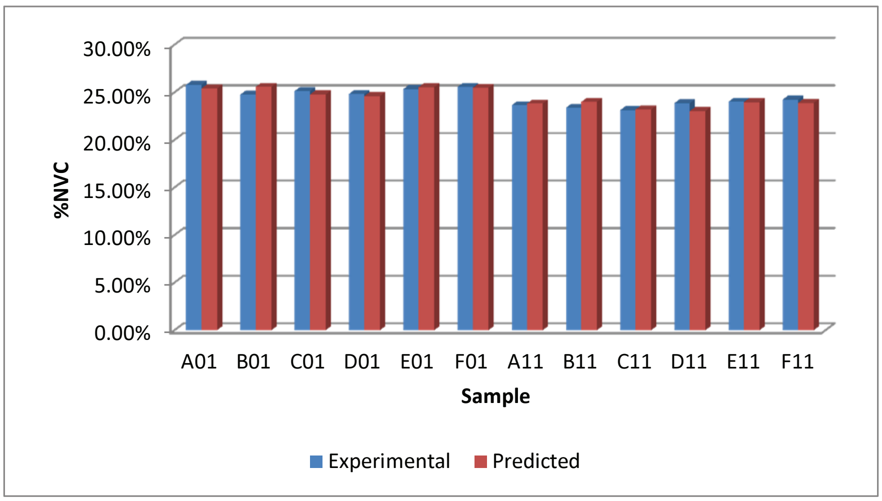
average error	0.48%

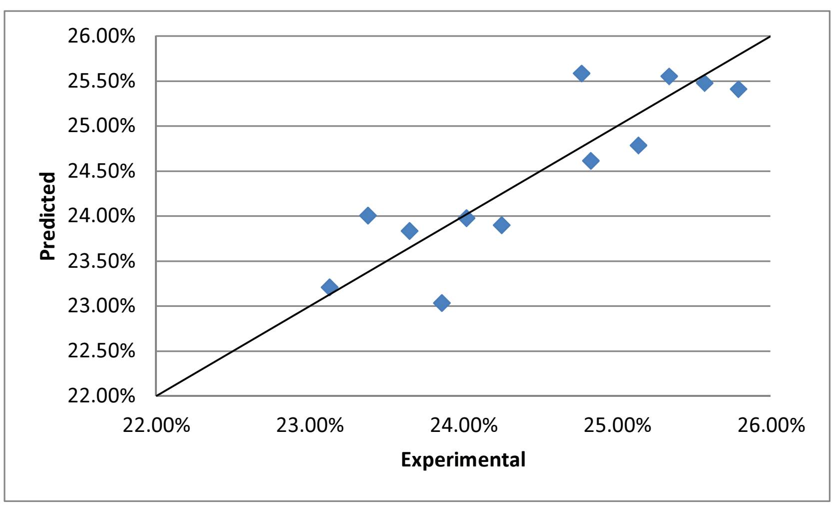




%NVC	Experimental	Predicted	95% CI Low	95% CI High	95% PI Low	95% PI High	%error
SCR - A01	25.79%	25.41%	25.25%	25.58%	24.59%	26.24%	1.49%
SCR - B01	24.77%	25.58%	25.42%	25.75%	24.76%	26.41%	3.18%
SCR - C01	25.14%	24.78%	24.62%	24.95%	23.96%	25.61%	1.43%
SCR - D01	24.83%	24.61%	24.44%	24.78%	23.79%	25.44%	0.88%
SCR - E01	25.34%	25.55%	25.37%	25.74%	24.73%	26.38%	0.84%
SCR - F01	25.57%	25.48%	25.33%	25.62%	24.66%	26.30%	0.36%
SCR - A11	23.65%	23.83%	23.59%	24.07%	22.99%	24.68%	0.77%
SCR - B11	23.38%	24.00%	23.76%	24.25%	23.16%	24.85%	2.60%
SCR - C11	23.13%	23.21%	22.96%	23.45%	22.36%	24.05%	0.33%
SCR - D11	23.86%	23.03%	22.79%	23.28%	22.19%	23.88%	3.59%
SCR - E11	24.02%	23.98%	23.72%	24.23%	23.13%	24.82%	0.19%
SCR - F11	24.25%	23.90%	23.67%	24.12%	23.06%	24.74%	1.47%

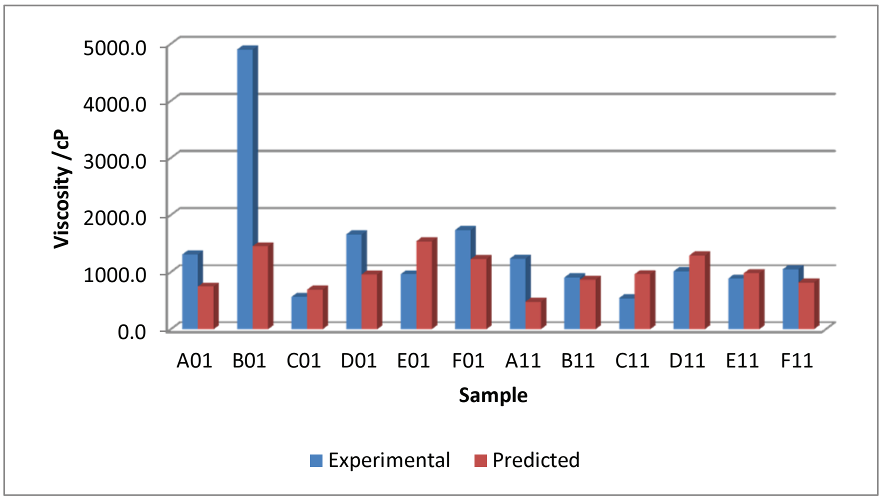
average error	1.43%

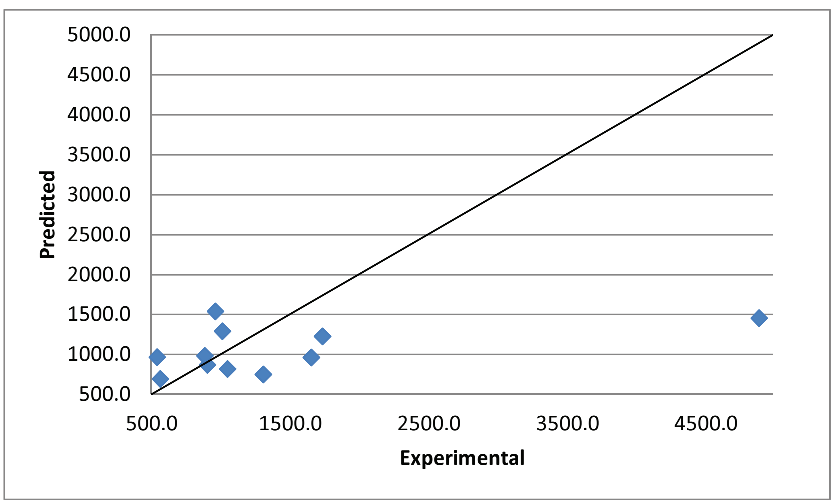




Viscosity	Experimental	Predicted	95% CI Low	95% CI High	95% PI Low	95% PI High	%error
SCR - A01	1312.0	749.0	561.2	1049.6	429.9	1620.0	75.16%
SCR - B01	4899.0	1453.4	937.8	2549.5	681.5	4991.9	237.06%
SCR - C01	567.9	693.2	514.5	984.3	401.8	1471.3	18.08%
SCR - D01	1660.0	960.3	662.8	1514.5	506.7	2471.9	72.86%
SCR - E01	963.8	1540.4	969.3	2817.5	704.7	5664.2	37.43%
SCR - F01	1740.0	1228.4	834.1	1985.9	611.6	3616.2	41.65%
SCR - A11	1236.0	481.5	388.5	612.2	307.5	859.0	156.71%
SCR - B11	907.8	869.2	669.8	1172.9	489.9	1948.0	4.45%
SCR - C11	543.9	964.7	730.3	1333.0	528.6	2289.9	43.62%
SCR - D11	1016.0	1291.1	958.3	1832.9	657.7	3598.6	21.30%
SCR - E11	887.8	982.5	742.1	1361.8	535.8	2355.4	9.64%
SCR - F11	1052.0	818.6	653.2	1055.8	472.7	1749.8	28.51%

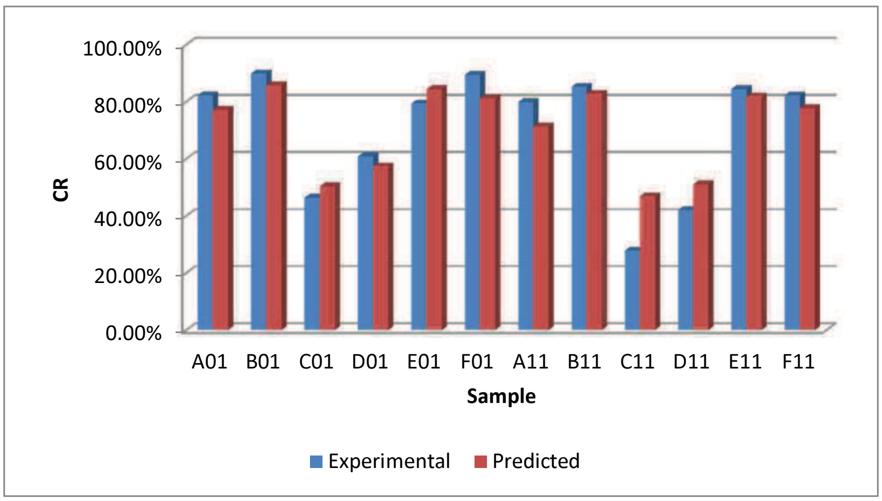
average error	62.21%

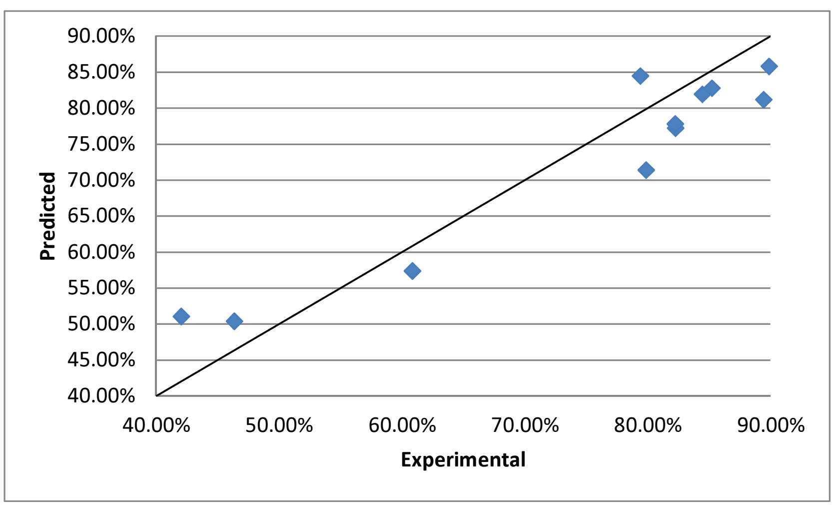




CR	Experimental	Predicted	95% CI Low	95% CI High	95% PI Low	95% PI High	%error
SCR - A01	82.26%	77.18%	75.19%	79.17%	68.46%	85.90%	6.58%
SCR - B01	89.89%	85.78%	83.60%	87.95%	77.02%	94.54%	4.79%
SCR - C01	46.38%	50.37%	48.36%	52.38%	41.65%	59.09%	7.92%
SCR - D01	60.87%	57.36%	55.27%	59.46%	48.62%	66.11%	6.11%
SCR - E01	79.39%	84.43%	82.02%	86.84%	75.61%	93.25%	5.97%
SCR - F01	89.43%	81.16%	79.43%	82.89%	72.50%	89.82%	10.19%
SCR - A11	79.88%	71.37%	67.15%	75.60%	61.89%	80.85%	11.92%
SCR - B11	85.22%	82.78%	78.66%	86.90%	73.34%	92.21%	2.95%
SCR - C11	27.85%	46.87%	42.77%	50.98%	37.44%	56.30%	40.58%
SCR - D11	42.06%	51.06%	46.86%	55.26%	41.59%	60.53%	17.63%
SCR - E11	84.44%	81.90%	77.66%	86.14%	72.41%	91.39%	3.10%
SCR - F11	82.23%	77.76%	74.03%	81.50%	68.49%	87.04%	5.74%

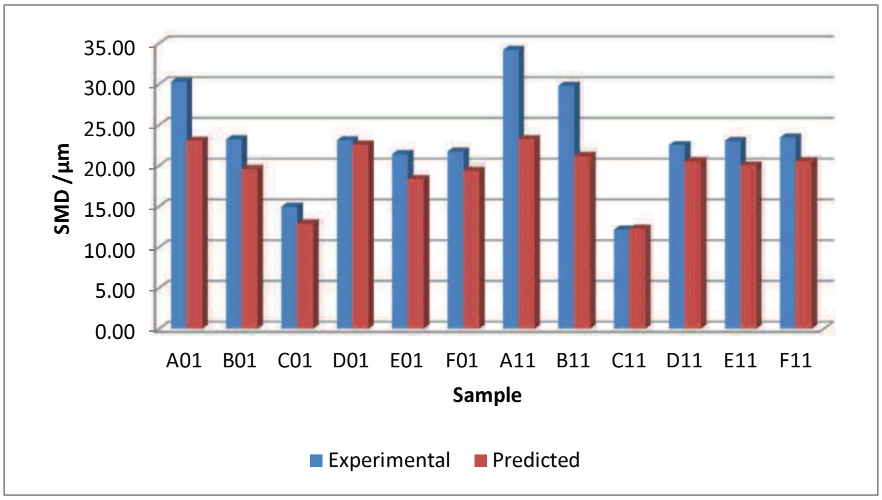
average error	10.29%

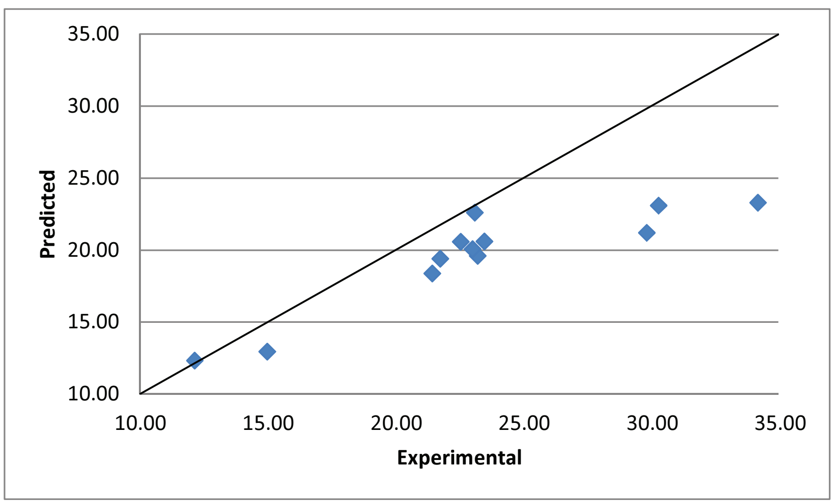




SMD	Experimental	Predicted	95% CI Low	95% CI High	95% PI Low	95% PI High	%error
SCR - A01	30.30	23.09	21.82	24.36	17.62	28.57	31.22%
SCR - B01	23.22	19.59	18.15	21.03	14.07	25.11	18.53%
SCR - C01	14.99	12.94	11.64	14.24	7.46	18.42	15.82%
SCR - D01	23.11	22.61	21.19	24.02	17.10	28.12	2.22%
SCR - E01	21.44	18.37	16.78	19.96	12.81	23.93	16.72%
SCR - F01	21.75	19.39	18.24	20.54	13.94	24.84	12.17%
SCR - A11	34.19	23.28	20.57	25.98	17.31	29.25	46.87%
SCR - B11	29.83	21.20	18.74	23.66	15.33	27.06	40.74%
SCR - C11	12.15	12.32	9.84	14.79	6.44	18.19	1.35%
SCR - D11	22.55	20.56	18.07	23.06	14.68	26.45	9.65%
SCR - E11	23.02	20.06	17.55	22.57	14.17	25.95	14.75%
SCR - F11	23.48	20.58	18.36	22.81	14.81	26.36	14.07%

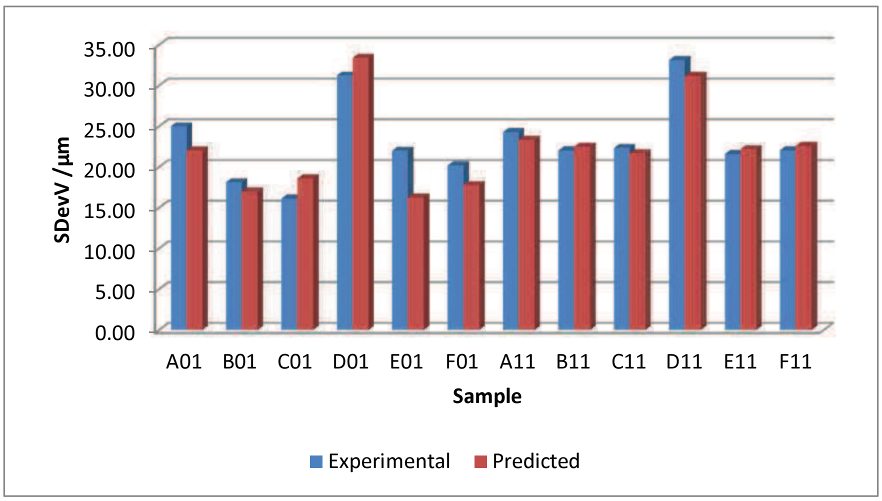
average error	18.68%

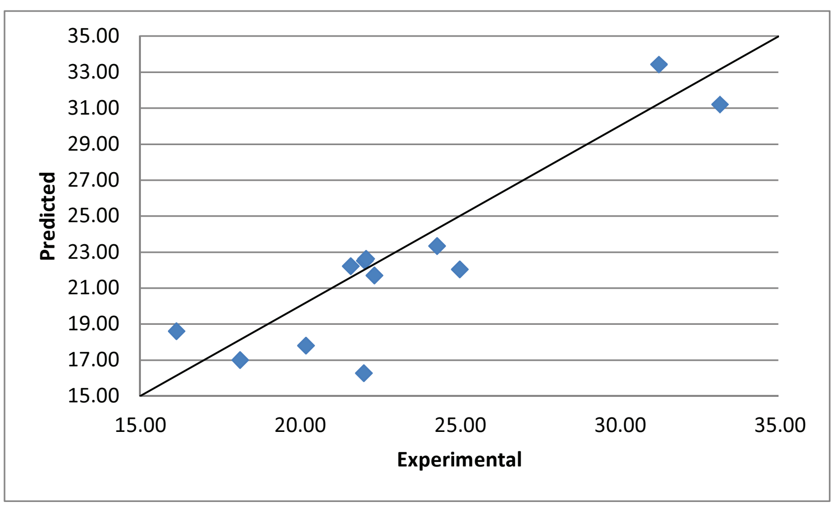




SDevV	Experimental	Predicted	95% CI Low	95% CI High	95% PI Low	95% PI High	%error
SCR - A01	25.01	22.03	20.18	24.04	15.18	31.97	13.54%
SCR - B01	18.14	17.00	15.50	18.65	11.70	24.71	6.69%
SCR - C01	16.15	18.60	17.05	20.30	12.82	26.99	13.17%
SCR - D01	31.25	33.42	30.53	36.58	23.01	48.53	6.48%
SCR - E01	22.01	16.26	14.68	18.02	11.16	23.70	35.33%
SCR - F01	20.20	17.79	16.52	19.16	12.30	25.75	13.52%
SCR - A11	24.30	23.33	19.11	28.49	15.43	35.28	4.14%
SCR - B11	22.04	22.52	18.71	27.10	14.99	33.82	2.12%
SCR - C11	22.34	21.70	18.18	25.92	14.50	32.48	2.93%
SCR - D11	33.16	31.19	26.00	37.41	20.80	46.77	6.32%
SCR - E11	21.60	22.21	18.40	26.82	14.77	33.41	2.75%
SCR - F11	22.08	22.62	19.19	26.66	15.20	33.67	2.40%

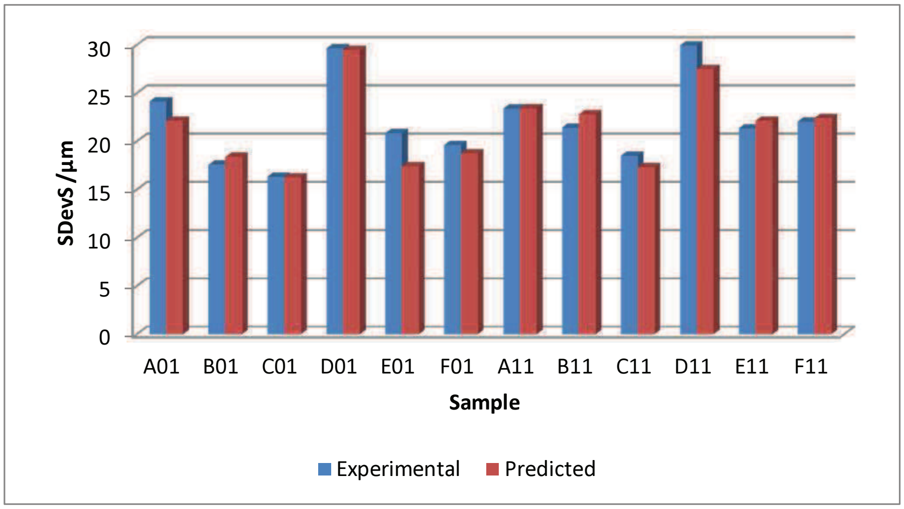
average error	9.12%

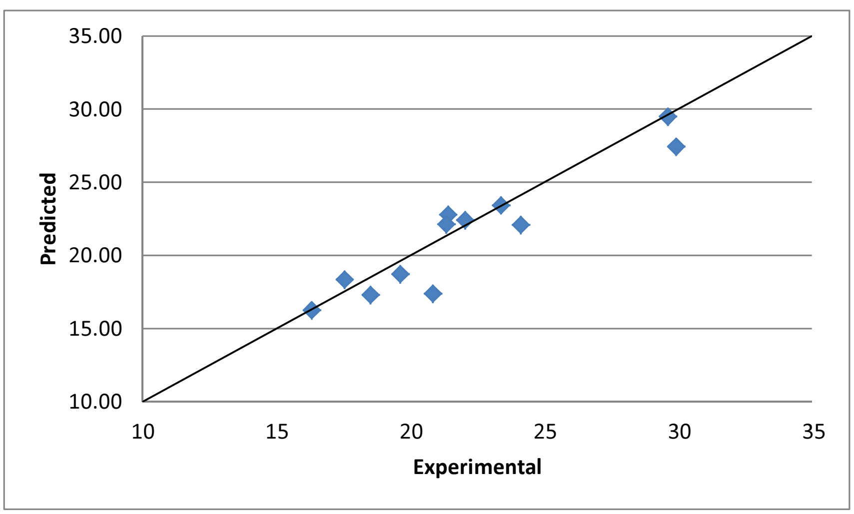




SDevS	Experimental	Predicted	95% CI Low	95% CI High	95% PI Low	95% PI High	%error
SCR - A01	24.13	22.09	20.92	23.26	17.11	27.08	9.22%
SCR - B01	17.55	18.37	17.06	19.68	13.35	23.39	4.45%
SCR - C01	16.32	16.26	15.08	17.43	11.27	21.24	0.39%
SCR - D01	29.62	29.49	28.23	30.74	24.48	34.49	0.45%
SCR - E01	20.84	17.40	15.95	18.86	12.35	22.46	19.74%
SCR - F01	19.62	18.72	17.68	19.77	13.77	23.68	4.80%
SCR - A11	23.38	23.43	20.91	25.95	17.97	28.89	0.21%
SCR - B11	21.42	22.80	20.41	25.19	17.40	28.20	6.05%
SCR - C11	18.51	17.32	14.92	19.71	11.91	22.72	6.89%
SCR - D11	29.93	27.45	25.10	29.81	22.06	32.84	9.03%
SCR - E11	21.34	22.14	19.66	24.62	16.69	27.58	3.61%
SCR - F11	22.05	22.42	20.28	24.55	17.12	27.71	1.63%

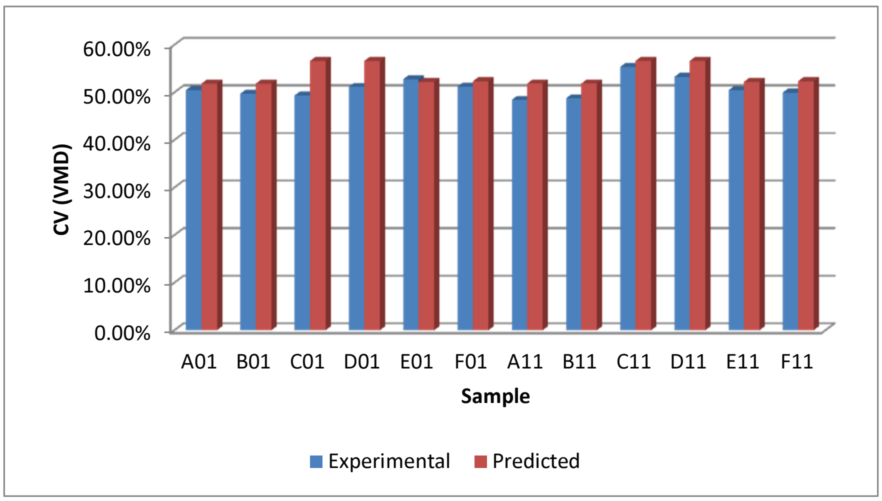
average error	5.54%

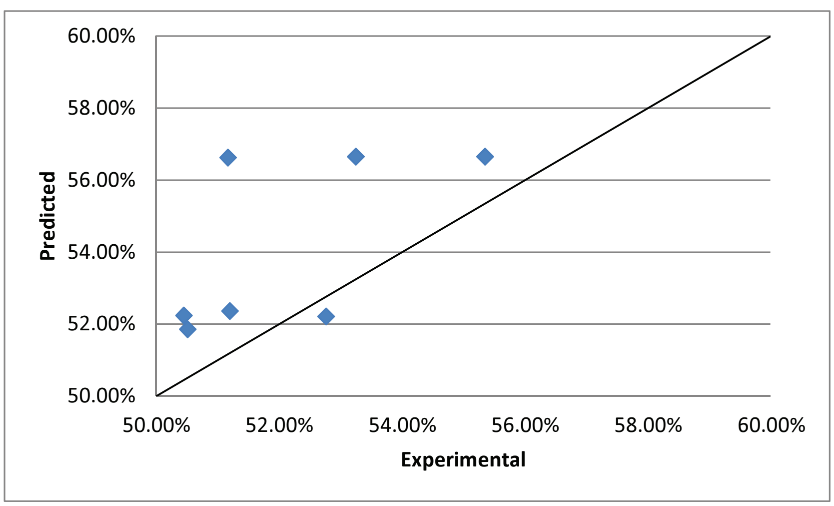




CV (VMD)	Experimental	Predicted	95% CI Low	95% CI High	95% PI Low	95% PI High	%error
SCR - A01	50.52%	51.85%	49.88%	53.82%	39.73%	63.97%	2.58%
SCR - B01	49.73%	51.85%	49.88%	53.82%	39.73%	63.97%	4.10%
SCR - C01	49.36%	56.62%	54.68%	58.56%	44.51%	68.74%	12.83%
SCR - D01	51.17%	56.62%	54.68%	58.56%	44.51%	68.74%	9.63%
SCR - E01	52.77%	52.21%	50.39%	54.04%	40.12%	64.31%	1.06%
SCR - F01	51.20%	52.36%	50.59%	54.13%	40.27%	64.45%	2.21%
SCR - A11	48.43%	51.87%	49.60%	54.15%	39.70%	64.04%	6.64%
SCR - B11	48.74%	51.87%	49.60%	54.15%	39.70%	64.04%	6.04%
SCR - C11	55.35%	56.64%	54.40%	58.89%	44.48%	68.81%	2.28%
SCR - D11	53.25%	56.64%	54.40%	58.89%	44.48%	68.81%	5.99%
SCR - E11	50.46%	52.23%	50.08%	54.38%	40.09%	64.38%	3.41%
SCR - F11	49.97%	52.38%	50.28%	54.48%	40.24%	64.52%	4.61%

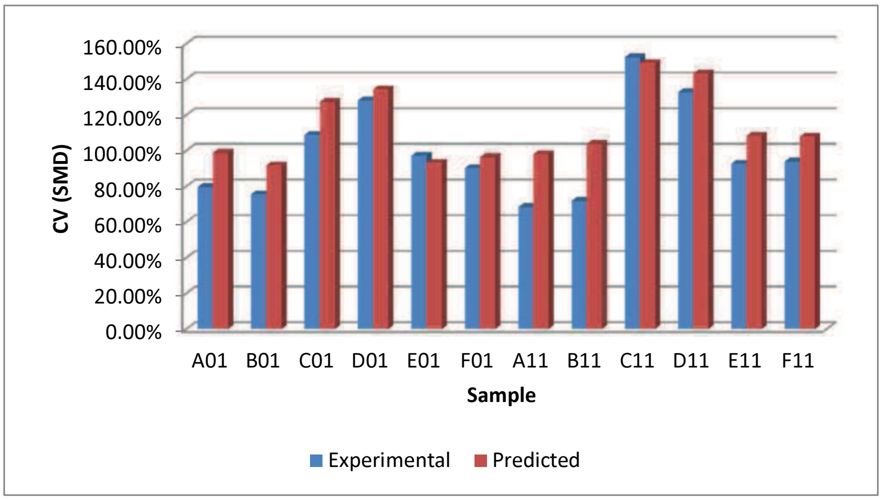
average error	5.12%

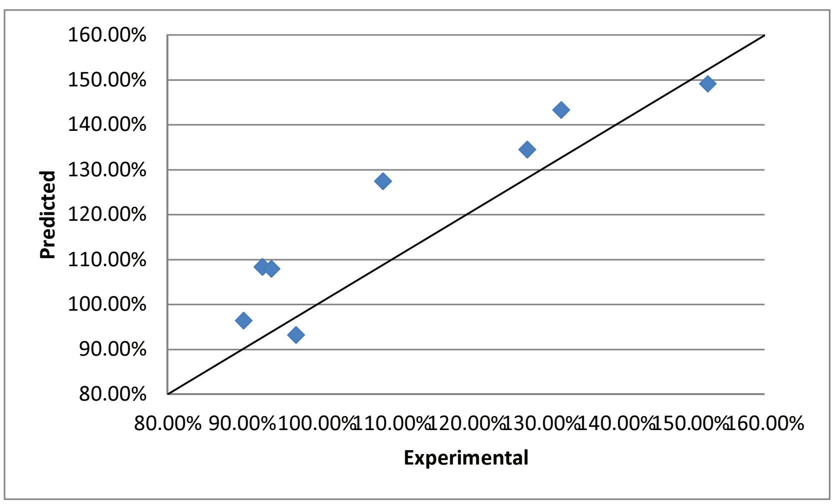




CV (SMD)	Experimental	Predicted	95% CI Low	95% CI High	95% PI Low	95% PI High	%error
SCR - A01	79.64%	98.83%	94.45%	103.20%	76.94%	120.71%	19.4 2%
SCR - B01	75.58%	91.77%	87.28%	96.26%	69.86%	113.68%	17.64 %
SCR - C01	108.87%	127.41%	122.88%	131.95%	105.50%	149.33%	14.55%
SCR - D01	128.17%	134.47%	129.98%	138.97%	112.56%	156.38%	4.69%
SCR - E01	97.20%	93.20%	88.30%	98.09%	71.20%	115.20%	4.29%
SCR - F01	90.21%	96.43%	92.57%	100.29%	74.64%	118.22%	6.45 %
SCR - A11	68.38%	98.06%	89.02%	107.10%	74.79%	121.33%	30.2 7%
SCR - B11	71.81%	103.85%	95.26%	112.44%	80.75%	126.95%	30. 85%
SCR - C11	152.35%	149.11%	140.11%	158.10%	125.85%	172.36%	2.17%
SCR - D11	132.73%	143.32%	134.28%	152.36%	120.05%	166.59%	7.39%
SCR - E11	92.70%	108.33%	99.24%	117.41%	85.04%	131.62%	14. 42%
SCR - F11	93.91%	107.96%	100.08%	115.84%	85.11%	130.81%	13 .02%

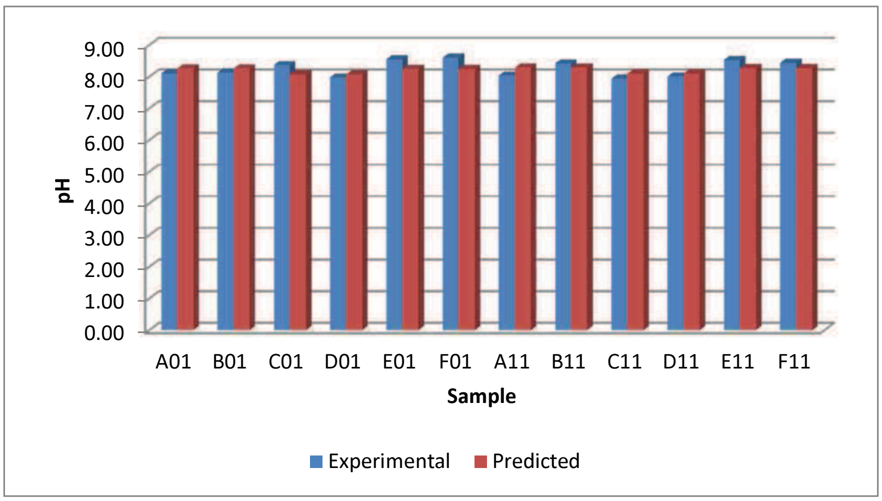
average error	13.76%

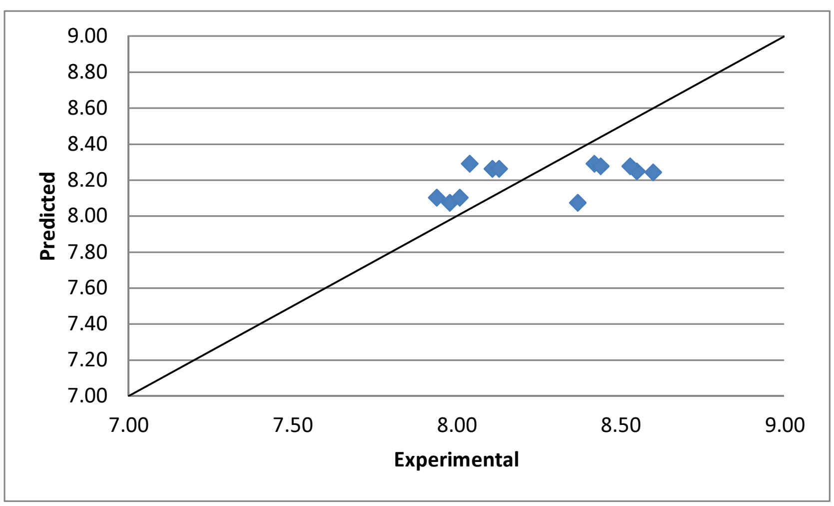




pH	Experimental	Predicted	95% CI Low	95% CI High	95% PI Low	95% PI High	%error
SCR - A01	8.11	8.26	8.17	8.35	7.71	8.81	1.84%
SCR - B01	8.13	8.26	8.17	8.35	7.71	8.81	1.59%
SCR - C01	8.37	8.07	7.99	8.16	7.53	8.62	3.66%
SCR - D01	7.98	8.07	7.99	8.16	7.53	8.62	1.17%
SCR - E01	8.55	8.25	8.17	8.33	7.70	8.79	3.67%
SCR - F01	8.60	8.24	8.16	8.32	7.70	8.79	4.35%
SCR - A11	8.04	8.29	8.16	8.42	7.73	8.85	3.02%
SCR - B11	8.42	8.29	8.16	8.42	7.73	8.85	1.57%
SCR - C11	7.94	8.10	7.97	8.23	7.55	8.66	2.01%
SCR - D11	8.01	8.10	7.97	8.23	7.55	8.66	1.14%
SCR - E11	8.53	8.28	8.15	8.40	7.72	8.83	3.07%
SCR - F11	8.44	8.28	8.15	8.40	7.72	8.83	1.98%

average error	2.42%





Appendix E.5 - Model Term Selection Method Comparison

Model Term Selection Comparison for the VMD Model

	Intercept	A	B	C	D	E	F	G	H	J	AB	AC	AD	AE	AG	AH	BD	BG	BH	CH	DG	DH	DJ	EG	EJ	FJ	GH	HJ
Backward	41.68	-2.61	-4.57	4.74	-0.05	5.39	-7.21	-0.04	3.50	8.03	-2.15	1.73	-0.55	-1.09	-1.71	3.70	1.79	-3.30	-2.17	-1.59	1.24	-1.37	1.25	-1.29	1.41	-2.03	-1.24	5.15
Forward	41.61	-2.62	-4.71	4.76	-0.11	5.53	-6.91	-0.23	3.74	8.19	-1.96	1.68			-1.77	3.85	1.84	-3.32	-1.96	-1.57	1.18	-1.27			1.33	-1.96		5.16
Stepwise	41.61	-2.62	-4.71	4.76	-0.11	5.53	-6.91	-0.23	3.74	8.19	-1.96	1.68			-1.77	3.85	1.84	-3.32	-1.96	-1.57	1.18	-1.27			1.33	-1.96		5.16

Response **5 VMD**

Backward Elimination Regression with Alpha to Exit = 0.100

Removed	Coefficient Estimate	t for H0 Coeff=0	Prob > |t|	R-Squared	MSE
D-Mass DI	-0.03	-0.04	0.97	0.96	25.30
CD	-0.10	-0.13	0.90	0.96	24.49
CF	-0.15	-0.21	0.84	0.96	23.76
CE	0.18	0.25	0.80	0.96	23.09
BE	0.21	0.30	0.76	0.96	22.47
AF	-0.31	-0.45	0.66	0.96	21.96
EH	-0.36	-0.55	0.59	0.96	21.53
G-Initial T	-0.36	-0.56	0.58	0.96	21.13
FG	-0.45	-0.64	0.52	0.96	20.80
CJ	0.53	0.81	0.43	0.96	20.62
BC	-0.59	-0.91	0.37	0.96	20.53
DF	-0.64	-1.05	0.30	0.96	20.58
AJ	0.60	1.02	0.31	0.95	20.61
DE	0.72	1.10	0.28	0.95	20.71
EF	-0.69	-1.08	0.29	0.95	20.79
GJ	-0.58	-0.99	0.33	0.95	20.77
BF	0.92	1.44	0.16	0.95	21.26
AD	-0.84	-1.35	0.19	0.95	21.63
FH	0.95	1.51	0.14	0.94	22.20
CG	0.87	1.38	0.17	0.94	22.61
BJ	0.79	1.25	0.22	0.94	22.87

Hierarchical Terms Added after Backward Elimination Regression
D-Mass DETA (Organic), G-Initial Temperature

ANOVA for Response Surface Reduced 2FI Model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	17648.25	27	653.6387	27.28531	**< 0.0001**	**significant**
A-Mass Po	436.7749	1	436.7749	18.23261	**< 0.0001**	
B-Mass St	1200.735	1	1200.735	50.12313	**< 0.0001**	
C-Mass LI	1339.613	1	1339.613	55.92042	**< 0.0001**	
D-Mass DI	0.137661	1	0.137661	0.005746	0.9399	
E-Mass W	1696.74	1	1696.74	70.82825	**< 0.0001**	
F-Stirrer S	2522.784	1	2522.784	105.3104	**< 0.0001**	
G-Initial T	0.090534	1	0.090534	0.003779	0.9512	
H-Acid Va	808.8206	1	808.8206	33.76318	**< 0.0001**	
J-Viscosity	4350.866	1	4350.866	181.6213	**< 0.0001**	
AB	230.2794	1	230.2794	9.61272	**0.0033**	
AC	145.9063	1	145.9063	6.090672	**0.0173**	
AD	17.26789	1	17.26789	0.720826	0.4002	
AE	68.25657	1	68.25657	2.849283	0.0980	
AG	161.3504	1	161.3504	6.735365	**0.0126**	
AH	804.1156	1	804.1156	33.56677	**< 0.0001**	
BD	184.5932	1	184.5932	7.705606	**0.0079**	
BG	612.402	1	612.402	25.56394	**< 0.0001**	
BH	281.055	1	281.055	11.73228	**0.0013**	
CH	156.6507	1	156.6507	6.539182	**0.0138**	
DG	85.386	1	85.386	3.564329	0.0652	
DH	108.504	1	108.504	4.529361	**0.0386**	
DJ	92.83581	1	92.83581	3.875312	0.0549	
EG	81.86771	1	81.86771	3.417463	0.0708	
EJ	118.2283	1	118.2283	4.935289	**0.0312**	
FJ	245.4925	1	245.4925	10.24777	**0.0025**	
GH	94.56173	1	94.56173	3.947358	**0.0528**	
HJ	1719.551	1	1719.551	71.78046	**< 0.0001**	
Residual	1125.918	47	23.9557			
Lack of Fit	1048.197	43	24.37668	1.254579	0.4663	not significant
Pure Error	77.72065	4	19.43016			
Cor Total	18774.16	74				

Std. Dev.	4.894	**R-Squared**	0.940
Mean	41.792	**Adj R-Squa**	0.906
C.V. %	11.711	**Pred R-Squ**	0.839
PRESS	3013.821	**Adeq Preci**	20.550

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	41.68367	1	0.581022	40.51481	42.85254	
A-Mass Pol	-2.61355	1	0.612077	-3.84489	-1.38221	1.108477
B-Mass Sty	-4.56749	1	0.645147	-5.86536	-3.26963	1.196746
C-Mass LM	4.74051	1	0.633928	3.465212	6.015809	1.137143
D-Mass DE	-0.04684	1	0.617835	-1.28976	1.196089	1.097564
E-Mass Wa	5.394759	1	0.641016	4.105201	6.684316	1.166373
F-Stirrer Sp	-7.21194	1	0.702775	-8.62574	-5.79814	1.397553
G-Initial Te	-0.03739	1	0.608237	-1.26101	1.186223	1.049312
H-Acid Valu	3.497233	1	0.60187	2.286426	4.70804	1.133916
J-Viscosity	8.03048	1	0.595879	6.831726	9.229234	1.111454
AB	-2.14619	1	0.692221	-3.53876	-0.75362	1.297751
AC	1.725618	1	0.699217	0.318975	3.132262	1.301803
AD	-0.55256	1	0.650826	-1.86185	0.756732	1.143408
AE	-1.08688	1	0.643895	-2.38223	0.208466	1.099338
AG	-1.70625	1	0.65745	-3.02887	-0.38363	1.154772
AH	3.703183	1	0.639176	2.417327	4.98904	1.210623
BD	1.786862	1	0.643706	0.491892	3.081832	1.124063
BG	-3.29683	1	0.652052	-4.60859	-1.98507	1.134943
BH	-2.16921	1	0.6333	-3.44324	-0.89517	1.154982
CH	-1.58838	1	0.621143	-2.83795	-0.3388	1.094314
DG	1.235909	1	0.654633	-0.08104	2.552861	1.143943
DH	-1.37482	1	0.645992	-2.67439	-0.07525	1.190591
DJ	1.250431	1	0.635194	-0.02741	2.528276	1.160104
EG	-1.29421	1	0.700087	-2.7026	0.114186	1.286494
EJ	1.41068	1	0.634998	0.133229	2.68813	1.140984
FJ	-2.03409	1	0.635412	-3.31237	-0.7558	1.146068
GH	-1.24232	1	0.625287	-2.50023	0.015598	1.108964
HJ	5.148134	1	0.607641	3.925719	6.370549	1.155763

Final Equation in Terms of Coded Factors:

VMD	=	
41.68367		41.68
-2.61355	* A	-2.61
-4.56749	* B	-4.57
4.74051	* C	4.74
-0.04684	* D	-0.05
5.394759	* E	5.39
-7.21194	* F	-7.21
-0.03739	* G	-0.04
3.497233	* H	3.50
8.03048	* J	8.03
-2.14619	* A * B	-2.15
1.725618	* A * C	1.73
-0.55256	* A * D	-0.55
-1.08688	* A * E	-1.09
-1.70625	* A * G	-1.71
3.703183	* A * H	3.70
1.786862	* B * D	1.79
-3.29683	* B * G	-3.30
-2.16921	* B * H	-2.17
-1.58838	* C * H	-1.59
1.235909	* D * G	1.24
-1.37482	* D * H	-1.37
1.250431	* D * J	1.25
-1.29421	* E * G	-1.29
1.41068	* E * J	1.41
-2.03409	* F * J	-2.03
-1.24232	* G * H	-1.24
5.148134	* H * J	5.15

Final Equation in Terms of Actual Factors:

VMD	=
-42.5575	
0.444493	* Mass Polyester
1.134193	* Mass Styrene
-1.30786	* Mass LMA
-23.9417	* Mass DETA (Organic)
0.044234	* Mass Water
0.285663	* Stirrer Speed
7.245392	* Initial Temperature
-4.00061	* Acid Value
-0.12004	* Viscosity
-0.00314	* Mass Polyester * Mass Styrene
0.016077	* Mass Polyester * Mass LMA
-0.01654	* Mass Polyester * Mass DETA (Organic)
-0.00045	* Mass Polyester * Mass Water
-0.00578	* Mass Polyester * Initial Temperature
0.008118	* Mass Polyester * Acid Value
0.121267	* Mass Styrene * Mass DETA (Organic)
-0.02534	* Mass Styrene * Initial Temperature
-0.01078	* Mass Styrene * Acid Value
-0.05021	* Mass LMA * Acid Value
0.194037	* Mass DETA (Organic) * Initial Temperature
-0.13962	* Mass DETA (Organic) * Acid Value
0.007493	* Mass DETA (Organic) * Viscosity
-0.0028	* Mass Water * Initial Temperature
0.000116	* Mass Water * Viscosity
-0.00021	* Stirrer Speed * Viscosity
-0.01429	* Initial Temperature * Acid Value
0.00226	* Acid Value * Viscosity

Response **5 VMD**

Forwa rd Regression with Alpha to Enter = 0.100

Added	Coefficient Estimate	t for H0 Coeff=0	Prob > |t|	R-Squared	MSE
J-Viscosity	8.84	5.76	<0.0001	0.31	176.90
E-Mass W	5.19	3.44	0.00	0.41	154.05
F-Stirrer S	-4.42	-3.10	0.00	0.48	137.64
HJ	5.04	4.02	0.00	0.58	113.45
B-Mass St	-4.08	-3.37	0.00	0.64	98.83
C-Mass LI	4.23	3.81	0.00	0.70	82.65
H-Acid Va	3.35	3.42	0.00	0.75	71.39
AH	3.58	3.76	0.00	0.79	59.70
BG	-2.62	-2.77	0.01	0.81	54.23
A-Mass Po	-2.33	-2.72	0.01	0.83	49.37
FJ	-2.31	-2.75	0.01	0.85	44.77
BH	-1.97	-2.52	0.01	0.86	41.27
BD	1.78	2.23	0.03	0.87	38.78
AG	-1.82	-2.29	0.03	0.88	36.27
CH	-1.55	-2.14	0.04	0.89	34.22
EJ	1.65	2.35	0.02	0.90	31.78
AC	1.40	1.86	0.07	0.91	30.48
AB	-1.55	-2.15	0.04	0.91	28.66
DH	-1.19	-1.74	0.09	0.92	27.67
DG	1.17	1.70	0.09	0.92	26.74

H ierarchical Terms Added after Forward Regression
D-Mass DETA (Organic), G-Initial Temperature

AN OVA for Response Surface Reduced 2FI Model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	17334.45	22	787.9296	28.45868	**< 0.0001**	**significant**
A-Mass Pol	441.2913	1	441.2913	15.93869	**0.0002**	
B-Mass Sty	1317.144	1	1317.144	47.573	**< 0.0001**	
C-Mass LM	1357.12	1	1357.12	49.01687	**< 0.0001**	
D-Mass DE	0.767664	1	0.767664	0.027727	0.8684	
E-Mass Wa	1815.299	1	1815.299	65.56551	**< 0.0001**	
F-Stirrer Sp	2586.854	1	2586.854	93.4328	**< 0.0001**	
G-Initial Te	3.506862	1	3.506862	0.126662	0.7234	
H-Acid Valu	953.9434	1	953.9434	34.45482	**< 0.0001**	
J-Viscosity	4580.235	1	4580.235	165.4303	**< 0.0001**	
AB	199.1664	1	199.1664	7.193553	**0.0098**	
AC	143.3698	1	143.3698	5.178275	**0.0270**	
AG	174.9093	1	174.9093	6.317428	**0.0151**	
AH	897.6127	1	897.6127	32.42025	**< 0.0001**	
BD	197.4021	1	197.4021	7.12983	**0.0101**	
BG	640.5545	1	640.5545	23.13574	**< 0.0001**	
BH	245.3244	1	245.3244	8.860701	**0.0044**	
CH	156.2713	1	156.2713	5.644255	**0.0212**	
DG	78.39437	1	78.39437	2.831472	0.0984	
DH	94.64585	1	94.64585	3.418448	0.0702	
EJ	107.8623	1	107.8623	3.895803	0.0537	
FJ	233.0103	1	233.0103	8.415936	**0.0054**	
HJ	1761.957	1	1761.957	63.6389	**< 0.0001**	
Residual	1439.713	52	27.68679			
Lack of Fit	1361.993	48	28.37484	1.46035	0.3940	not significant
Pure Error	77.72065	4	19.43016			
Cor Total	18774.16	74				

Std. Dev.	5.262	**R-Squared**	0.923
Mean	41.792	**Adj R-Squa**	0.891
C.V. %	12.590	**Pred R-Squ**	0.837
PRESS	3052.470	**Adeq Preci**	21.319

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	41.60576	1	0.619429	40.36278	42.84873	
A-Mass Pol	-2.62046	1	0.656374	-3.93757	-1.30335	1.102947
B-Mass Sty	-4.71476	1	0.683564	-6.08643	-3.34309	1.162461
C-Mass LM	4.756532	1	0.679388	3.393241	6.119823	1.130074
D-Mass DE	-0.10963	1	0.658412	-1.43083	1.211565	1.078489
E-Mass Wa	5.528811	1	0.682801	4.158671	6.898951	1.14505
F-Stirrer Sp	-6.90988	1	0.71486	-8.34435	-5.47541	1.251162
G-Initial Te	-0.23099	1	0.649045	-1.5334	1.071411	1.03382
H-Acid Valu	3.741643	1	0.637437	2.462532	5.020755	1.10049
J-Viscosity	8.190731	1	0.636818	6.912863	9.4686	1.098352
AB	-1.95809	1	0.730063	-3.42307	-0.49311	1.248991
AC	1.676	1	0.736515	0.198075	3.153925	1.249742
AG	-1.77262	1	0.705252	-3.18781	-0.35742	1.149732
AH	3.849352	1	0.676051	2.492757	5.205948	1.171826
BD	1.837814	1	0.688275	0.456689	3.218938	1.111925
BG	-3.31611	1	0.689424	-4.69954	-1.93267	1.097788
BH	-1.96303	1	0.659466	-3.28634	-0.63971	1.083621
CH	-1.57269	1	0.66197	-2.90103	-0.24434	1.075406
DG	1.17933	1	0.700857	-0.22704	2.585701	1.134498
DH	-1.27341	1	0.688738	-2.65546	0.108643	1.170987
EJ	1.325626	1	0.671618	-0.02207	2.673326	1.104375
FJ	-1.96155	1	0.676157	-3.31836	-0.60474	1.122876
HJ	5.157941	1	0.646569	3.860505	6.455378	1.132248

Final Equation in Terms of Coded Factors:

VMD	=
41.60576	
-2.62046	* A
-4.71476	* B
4.756532	* C
-0.10963	* D
5.528811	* E
-6.90988	* F
-0.23099	* G
3.741643	* H
8.190731	* J
-1.95809	* A * B
1.676	* A * C
-1.77262	* A * G
3.849352	* A * H
1.837814	* B * D
-3.31611	* B * G
-1.96303	* B * H
-1.57269	* C * H
1.17933	* D * G
-1.27341	* D * H
1.325626	* E * J
-1.96155	* F * J
5.157941	* H * J

Final Equation in Terms of Actual Factors:

VMD	=
130.3175	
-0.11849	* Mass Polyester
0.993815	* Mass Styrene
-1.18007	* Mass LMA
-14.0347	* Mass DETA (Organic)
-0.13736	* Mass Water
0.276373	* Stirrer Speed
3.948699	* Initial Temperature
-4.57591	* Acid Value
-0.08293	* Viscosity
-0.00287	* Mass Polyester * Mass Styrene
0.015614	* Mass Polyester * Mass LMA
-0.00601	* Mass Polyester * Initial T emperature
0.008439	* Mass Polyester * Acid Value
0.124725	* Mass Styrene * Mass DETA (Organic)
-0.02548	* Mass Styrene * Initial Temperature
-0.00976	* Mass Styrene * Acid Value
-0.04971	* Mass LMA * Acid Value
0.185154	* Mass DETA (Organic) * Initial Temperature
-0.12932	* Mass DETA (Organic) * Acid Value
0.000109	* Mass Water * Viscosit y
-0.0002	* Stirrer Speed * Viscosity
0.002264	* Acid Value * Viscosity

Response **5 VMD**

Stepwise Regression with Alpha to Enter = 0.100, Alpha to Exit = 0.100

Added	Coefficient Estimate	t for H0 Coeff=0	Prob > |t|	R-Squared	MSE
J-Viscosity	8.84	5.76	<0.0001	0.31	176.90
E-Mass W	5.19	3.44	0.00	0.41	154.05
F-Stirrer S	-4.42	-3.10	0.00	0.48	137.64
HJ	5.04	4.02	0.00	0.58	113.45
B-Mass St	-4.08	-3.37	0.00	0.64	98.83
C-Mass LI	4.23	3.81	0.00	0.70	82.65
H-Acid Va	3.35	3.42	0.00	0.75	71.39
AH	3.58	3.76	0.00	0.79	59.70
BG	-2.62	-2.77	0.01	0.81	54.23
A-Mass Po	-2.33	-2.72	0.01	0.83	49.37
FJ	-2.31	-2.75	0.01	0.85	44.77
BH	-1.97	-2.52	0.01	0.86	41.27
BD	1.78	2.23	0.03	0.87	38.78
AG	-1.82	-2.29	0.03	0.88	36.27
CH	-1.55	-2.14	0.04	0.89	34.22
EJ	1.65	2.35	0.02	0.90	31.78
AC	1.40	1.86	0.07	0.91	30.48
AB	-1.55	-2.15	0.04	0.91	28.66
DH	-1.19	-1.74	0.09	0.92	27.67
DG	1.17	1.70	0.09	0.92	26.74

Hierarchical Terms Added after StepWise Regression
D-Mass DETA (Organic), G-Initial Temperature

ANOVA for Res ponse Surface Reduced 2FI Model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	17334.45	22	787.9296	28.45868	**< 0.0001**	**significant**
A-Mass Pol	441.2913	1	441.2913	15.93869	**0.0002**	
B-Mass Sty	1317.144	1	1317.144	47.573	**< 0.0001**	
C-Mass LM	1357.12	1	1357.12	49.01687	**< 0.0001**	
D-Mass DE	0.767664	1	0.767664	0.027727	0.8684	
E-Mass Wa	1815.299	1	1815.299	65.56551	**< 0.0001**	
F-Stirrer Sp	2586.854	1	2586.854	93.4328	**< 0.0001**	
G-Initial Te	3.506862	1	3.506862	0.126662	0.7234	
H-Acid Valu	953.9434	1	953.9434	34.45482	**< 0.0001**	
J-Viscosity	4580.235	1	4580.235	165.4303	**< 0.0001**	
AB	199.1664	1	199.1664	7.193553	**0.0098**	
AC	143.3698	1	143.3698	5.178275	**0.0270**	
AG	174.9093	1	174.9093	6.317428	**0.0151**	
AH	897.6127	1	897.6127	32.42025	**< 0.0001**	
BD	197.4021	1	197.4021	7.12983	**0.0101**	
BG	640.5545	1	640.5545	23.13574	**< 0.0001**	
BH	245.3244	1	245.3244	8.860701	**0.0044**	
CH	156.2713	1	156.2713	5.644255	**0.0212**	
DG	78.39437	1	78.39437	2.831472	0.0984	
DH	94.64585	1	94.64585	3.418448	0.0702	
EJ	107.8623	1	107.8623	3.895803	0.0537	
FJ	233.0103	1	233.0103	8.415936	**0.0054**	
HJ	1761.957	1	1761.957	63.6389	**< 0.0001**	
Residual	1439.713	52	27.68679			
Lack of Fit	1361.993	48	28.37484	1.46035	0.3940	not significant
Pure Error	77.72065	4	19.43016			
Cor Total	18774.16	74				

Std. Dev.	5.262	**R-Squared**	0.923
Mean	41.792	**Adj R-Squa**	0.891
C.V. %	12.590	**Pred R-Squ**	0.837
PRESS	3052.470	**Adeq Preci**	21.319

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	41.60576	1	0.619429	40.36278	42.84873	
A-Mass Pol	-2.62046	1	0.656374	-3.93757	-1.30335	1.102947
B-Mass Sty	-4.71476	1	0.683564	-6.08643	-3.34309	1.162461
C-Mass LM	4.756532	1	0.679388	3.393241	6.119823	1.130074
D-Mass DE	-0.10963	1	0.658412	-1.43083	1.211565	1.078489
E-Mass Wa	5.528811	1	0.682801	4.158671	6.898951	1.14505
F-Stirrer Sp	-6.90988	1	0.71486	-8.34435	-5.47541	1.251162
G-Initial Te	-0.23099	1	0.649045	-1.5334	1.071411	1.03382
H-Acid Valu	3.741643	1	0.637437	2.462532	5.020755	1.10049
J-Viscosity	8.190731	1	0.636818	6.912863	9.4686	1.098352
AB	-1.95809	1	0.730063	-3.42307	-0.49311	1.248991
AC	1.676	1	0.736515	0.198075	3.153925	1.249742
AG	-1.77262	1	0.705252	-3.18781	-0.35742	1.149732
AH	3.849352	1	0.676051	2.492757	5.205948	1.171826
BD	1.837814	1	0.688275	0.456689	3.218938	1.111925
BG	-3.31611	1	0.689424	-4.69954	-1.93267	1.097788
BH	-1.96303	1	0.659466	-3.28634	-0.63971	1.083621
CH	-1.57269	1	0.66197	-2.90103	-0.24434	1.075406
DG	1.17933	1	0.700857	-0.22704	2.585701	1.134498
DH	-1.27341	1	0.688738	-2.65546	0.108643	1.170987
EJ	1.325626	1	0.671618	-0.02207	2.673326	1.104375
FJ	-1.96155	1	0.676157	-3.31836	-0.60474	1.122876
HJ	5.157941	1	0.646569	3.860505	6.455378	1.132248

Final Equation in Terms of Coded Factors:

VMD	=
41.60576	
-2.62046	* A
-4.71476	* B
4.756532	* C
-0.10963	* D
5.528811	* E
-6.90988	* F
-0.23099	* G
3.741643	* H
8.190731	* J
-1.95809	* A * B
1.676	* A * C
-1.77262	* A * G
3.849352	* A * H
1.837814	* B * D
-3.31611	* B * G
-1.96303	* B * H
-1.57269	* C * H
1.17933	* D * G
-1.27341	* D * H
1.325626	* E * J
-1.96155	* F * J
5.157941	* H * J

Final Equation in Terms of Actual Factors:

VMD	=
130.3175	
-0.11849	* Mass Polyester
0.993815	* Mass Styrene
-1.18007	* Mass LMA
-14.0347	* Mass DETA (Organic)
-0.13736	* Mass Water
0.276373	* Stirrer Speed
3.948699	* Initial Temperature
-4.57591	* Acid Value
-0.08293	* Viscosity
-0.00287	* Mass Polyester * Mass Styrene
0.015614	* Mass Polyester * Mass LMA
-0.00601	* Mass Polyester * Initial Temperature
0.008439	* Mass Polyester * Acid Value
0.124725	* Mass Styrene * Mass DETA (Organic)
-0.02548	* Mass Styrene * Initial Temperature
-0.00976	* Mass Styrene * Acid Value
-0.04971	* Mass LMA * Acid Value
0.185154	* Mass DETA (Orga nic) * Initial Temperature
-0.12932	* Mass DETA (Organic) * Acid Value
0.000109	* Mass Water * Viscosity
-0.0002	* Stirrer Speed * Viscosity
0.002264	* Acid Value * Viscosity

Model Term Selection Comparison for the Buildup Model

	Intercept	A	B	C	D	E	F	G	H	J	AE	BE	BG	BH	CD	CH	DE	DH	EG	EH	EJ	FJ	GH	GJ
Backward	-1.07	-0.10	1.01	0.29	0.39	-0.36	0.10	-0.33	0.02	-0.42	0.35	-0.32	0.52	0.36	0.45	-0.43	0.30	0.48	-0.46	-0.32	0.30	-0.32	0.56	-0.33
Forward	-1.07	-0.10	1.01	0.29	0.39	-0.36	0.10	-0.33	0.02	-0.42	0.35	-0.32	0.52	0.36	0.45	-0.43	0.30	0.48	-0.46	-0.32	0.30	-0.32	0.56	-0.33
Stepwise	-1.07	-0.10	1.01	0.29	0.39	-0.36	0.10	-0.33	0.02	-0.42	0.35	-0.32	0.52	0.36	0.45	-0.43	0.30	0.48	-0.46	-0.32	0.30	-0.32	0.56	-0.33

Response **1 Buildup**
Transform: Natural log Constant: 0.05
Backward Elimination Regression with Alpha to Exit = 0.100

Removed	Coefficient Estimate	t for H0 Coeff=0	Prob > |t|	R-Squared	MSE
AC	0.01	-0.05	0.96	0.88	1.07
AJ	0.01	-0.07	0.95	0.88	1.03
BD	0.01	-0.10	0.92	0.88	1.00
AH	0.02	-0.13	0.90	0.88	0.97
CF	-0.02	0.15	0.88	0.88	0.95
AD	-0.02	0.16	0.88	0.88	0.92
CE	0.03	-0.19	0.85	0.88	0.89
DJ	0.02	-0.17	0.86	0.88	0.87
DF	0.04	-0.32	0.75	0.88	0.85
H-Acid Va	0.05	-0.40	0.69	0.88	0.83
BC	0.06	-0.45	0.66	0.88	0.82
HJ	-0.05	0.44	0.66	0.88	0.80
EF	-0.07	0.56	0.58	0.87	0.79
BF	0.08	-0.61	0.55	0.87	0.77
CJ	0.07	-0.59	0.56	0.87	0.76
AB	0.09	-0.75	0.46	0.87	0.76
CG	-0.09	0.79	0.44	0.87	0.75
AF	-0.10	0.84	0.41	0.87	0.74
A-Mass Po	-0.09	0.82	0.42	0.87	0.74
FH	0.12	-1.10	0.28	0.86	0.74
F-Stirrer S	0.17	-1.45	0.15	0.86	0.76
BJ	-0.16	1.40	0.17	0.85	0.77
DG	-0.16	1.43	0.16	0.84	0.79
AG	0.19	-1.62	0.11	0.84	0.81
FG	0.20	-1.55	0.13	0.83	0.83

Hierarchical Terms Added after Backward Elimination Regression
A-Mass Polyester, F-Stirrer Speed, H-Acid Value

ANOVA for Response Surface Reduced 2FI Model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	219.1916	23	9.530069	11.09188	**< 0.0001**	significant
A-Mass Po	0.629018	1	0.629018	0.732103	0.3962	
B-Mass St	63.97659	1	63.97659	74.46121	**< 0.0001**	
C-Mass LM	5.386456	1	5.386456	6.2692	**0.0155**	
D-Mass D	9.019256	1	9.019256	10.49735	**0.0021**	
E-Mass W	7.718523	1	7.718523	8.98345	**0.0042**	
F-Stirrer S	0.524516	1	0.524516	0.610474	0.4382	
G-Initial T	6.745715	1	6.745715	7.851217	**0.0072**	
H-Acid Va	0.019535	1	0.019535	0.022737	0.8807	
J-Viscosity	12.2884	1	12.2884	14.30225	**0.0004**	
AE	7.158903	1	7.158903	8.332119	**0.0057**	
BE	5.800442	1	5.800442	6.751031	**0.0122**	
BG	15.88669	1	15.88669	18.49023	**< 0.0001**	
BH	8.428533	1	8.428533	9.809819	**0.0029**	
CD	11.16352	1	11.16352	12.99302	**0.0007**	
CH	11.51702	1	11.51702	13.40445	**0.0006**	
DE	4.885755	1	4.885755	5.686443	**0.0209**	
DH	13.42402	1	13.42402	15.62397	**0.0002**	
EG	10.10661	1	10.10661	11.76291	**0.0012**	
EH	6.058113	1	6.058113	7.05093	**0.0105**	
EJ	5.581213	1	5.581213	6.495874	**0.0139**	
FJ	6.232448	1	6.232448	7.253835	**0.0096**	
GH	19.59559	1	19.59559	22.80695	**< 0.0001**	
GJ	6.495239	1	6.495239	7.559692	**0.0082**	
Residual	43.81887	51	0.859194			
Lack of Fit	43.73995	47	0.930637	47.16603	**0.0009**	significant
Pure Error	0.078924	4	0.019731			
Cor Total	263.0105	74				

Std. Dev.	0.927	**R-Squared**	0.833
Mean	-0.945	**Adj R-Squa**	0.758
C.V. %	98.116	**Pred R-Squ**	0.654
PRESS	91.054	**Adeq Preci**	11.601

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	-1.07018	1	0.109468	-1.28994	-0.85041	
A-Mass Pol	-0.09837	1	0.114973	-0.32919	0.132444	1.090505
B-Mass Sty	1.007999	1	0.116814	0.773485	1.242513	1.093936
C-Mass LM	0.29226	1	0.116725	0.057925	0.526595	1.07493
D-Mass DE	0.385746	1	0.119059	0.146725	0.624766	1.136383
E-Mass Wa	-0.35678	1	0.119037	-0.59576	-0.11781	1.121462
F-Stirrer Sp	0.095403	1	0.122104	-0.14973	0.340537	1.176282
G-Initial Te	-0.3271	1	0.116739	-0.56147	-0.09274	1.077727
H-Acid Valu	0.017392	1	0.115344	-0.21417	0.248955	1.161133
J-Viscosity	-0.42199	1	0.111584	-0.64601	-0.19798	1.08667
AE	0.351893	1	0.121908	0.107152	0.596634	1.098716
BE	-0.31932	1	0.122897	-0.56605	-0.07259	1.121305
BG	0.522104	1	0.121419	0.278346	0.765862	1.097232
BH	0.364683	1	0.116435	0.130929	0.598437	1.088541
CD	0.449933	1	0.124822	0.199341	0.700524	1.159609
CH	-0.43049	1	0.117582	-0.66655	-0.19444	1.093345
DE	0.304832	1	0.127832	0.048198	0.561467	1.217225
DH	0.477266	1	0.120744	0.234863	0.719669	1.159725
EG	-0.45625	1	0.133029	-0.72332	-0.18918	1.295126
EH	-0.32154	1	0.121093	-0.56465	-0.07844	1.156879
EJ	0.304859	1	0.119613	0.064725	0.544993	1.12879
FJ	-0.32207	1	0.119582	-0.56214	-0.082	1.131747
GH	0.556687	1	0.116567	0.322668	0.790706	1.074564
GJ	-0.32944	1	0.119818	-0.56998	-0.08889	1.135328

Final Equation in Terms of Coded Factors:

Ln(Buildup =
-1.07018
-0.09837 * A
1.007999 * B
0.29226 * C
0.385746 * D
-0.35678 * E
0.095403 * F
-0.3271 * G
0.017392 * H
-0.42199 * J
0.351893 * A * E
-0.31932 * B * E
0.522104 * B * G
0.364683 * B * H
0.449933 * C * D
-0.43049 * C * H
0.304832 * D * E
0.477266 * D * H
-0.45625 * E * G
-0.32154 * E * H
0.304859 * E * J
-0.32207 * F * J
0.556687 * G * H
-0.32944 * G * J

Final Equation in Terms of Actual Factors:

Ln(Buildup =
50.38058
-0.15158 * Mass Polyester
0.208857 * Mass Styrene
-0.22421 * Mass LMA
-9.93376 * Mass DETA (Organic)
-0.05356 * Mass Water
0.069977 * Stirrer Speed
0.738337 * Initial Temperature
0.089807 * Acid Value
-0.0115 * Viscosity
0.000145 * Mass Polyester * Mass Water
-0.0003 * Mass Styrene * Mass Water
0.004012 * Mass Styrene * Initial Temperature
0.001813 * Mass Styrene * Acid Value
0.194178 * Mass LMA * Mass DETA (Organic)
-0.01361 * Mass LMA * Acid Value
0.005814 * Mass DETA (Organic) * Mass Water
0.048467 * Mass DETA (Organic) * Acid Value
-0.00099 * Mass Water * Initial Temperature
-0.00045 * Mass Water * Acid Value
2.51E-05 * Mass Water * Viscosity
-3.3E-05 * Stirrer Speed * Viscosity
0.006401 * Initial Temperature * Acid Value
-0.00022 * Initial Temperature * Viscosity

Response **1 Buildup**
Transform: Natural log Constant: 0.05
Forward Regression with Alpha to Enter = 0.100

Added	Coefficient Estimate	t for H0 Coeff=0	Prob > |t|	R-Squared	MSE
B-Mass St	0.94	-4.69	<0.0001	0.23	2.77
E-Mass W	-0.50	2.55	0.01	0.30	2.57
J-Viscosity	-0.42	2.34	0.02	0.35	2.42
GH	0.44	-2.39	0.02	0.40	2.27
D-Mass D	0.44	-2.49	0.02	0.45	2.11
BG	0.46	-2.57	0.01	0.49	1.96
G-Initial T	-0.41	2.50	0.01	0.54	1.82
DH	0.38	-2.34	0.02	0.57	1.70
EH	-0.33	2.06	0.04	0.60	1.62
CH	-0.32	2.11	0.04	0.63	1.54
C-Mass LM	0.32	-2.17	0.03	0.65	1.46
AE	0.29	-1.89	0.06	0.67	1.40
CD	0.29	-1.96	0.05	0.69	1.34
EG	-0.32	2.18	0.03	0.71	1.26
BH	0.30	-2.28	0.03	0.74	1.18
EJ	0.28	-2.11	0.04	0.75	1.11
FJ	-0.27	2.07	0.04	0.77	1.05
BE	-0.31	2.36	0.02	0.79	0.97
GJ	-0.27	2.26	0.03	0.81	0.91
DE	0.30	-2.41	0.02	0.83	0.83

Hierarchical Terms Added after Forward Regression
A-Mass Polyester, F-Stirrer Speed, H-Acid Value

ANOVA for Response Surface Reduced 2FI Model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	219.1916	23	9.530069	11.09188	**< 0.0001**	significant
A-Mass Pol	0.629018	1	0.629018	0.732103	0.3962	
B-Mass Sty	63.97659	1	63.97659	74.46121	**< 0.0001**	
C-Mass LM	5.386456	1	5.386456	6.2692	**0.0155**	
D-Mass DE	9.019256	1	9.019256	10.49735	**0.0021**	
E-Mass Wa	7.718523	1	7.718523	8.98345	**0.0042**	
F-Stirrer Sp	0.524516	1	0.524516	0.610474	0.4382	
G-Initial Te	6.745715	1	6.745715	7.851217	**0.0072**	
H-Acid Valu	0.019535	1	0.019535	0.022737	0.8807	
J-Viscosity	12.2884	1	12.2884	14.30225	**0.0004**	
AE	7.158903	1	7.158903	8.332119	**0.0057**	
BE	5.800442	1	5.800442	6.751031	**0.0122**	
BG	15.88669	1	15.88669	18.49023	**< 0.0001**	
BH	8.428533	1	8.428533	9.809819	**0.0029**	
CD	11.16352	1	11.16352	12.99302	**0.0007**	
CH	11.51702	1	11.51702	13.40445	**0.0006**	
DE	4.885755	1	4.885755	5.686443	**0.0209**	
DH	13.42402	1	13.42402	15.62397	**0.0002**	
EG	10.10661	1	10.10661	11.76291	**0.0012**	
EH	6.058113	1	6.058113	7.05093	**0.0105**	
EJ	5.581213	1	5.581213	6.495874	**0.0139**	
FJ	6.232448	1	6.232448	7.253835	**0.0096**	
GH	19.59559	1	19.59559	22.80695	**< 0.0001**	
GJ	6.495239	1	6.495239	7.559692	**0.0082**	
Residual	43.81887	51	0.859194			
Lack of Fit	43.73995	47	0.930637	47.16603	**0.0009**	significant
Pure Error	0.078924	4	0.019731			
Cor Total	263.0105	74				

Std. Dev.	0.927	**R-Squared**	0.833
Mean	-0.945	**Adj R-Squa**	0.758
C.V. %	98.116	**Pred R-Squ**	0.654
PRESS	91.054	**Adeq Preci**	11.601

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	-1.07018	1	0.109468	-1.28994	-0.85041	
A-Mass Pol	-0.09837	1	0.114973	-0.32919	0.132444	1.090505
B-Mass Sty	1.007999	1	0.116814	0.773485	1.242513	1.093936
C-Mass LM	0.29226	1	0.116725	0.057925	0.526595	1.07493
D-Mass DE	0.385746	1	0.119059	0.146725	0.624766	1.136383
E-Mass Wa	-0.35678	1	0.119037	-0.59576	-0.11781	1.121462
F-Stirrer Sp	0.095403	1	0.122104	-0.14973	0.340537	1.176282
G-Initial Te	-0.3271	1	0.116739	-0.56147	-0.09274	1.077727
H-Acid Valu	0.017392	1	0.115344	-0.21417	0.248955	1.161133
J-Viscosity	-0.42199	1	0.111584	-0.64601	-0.19798	1.08667
AE	0.351893	1	0.121908	0.107152	0.596634	1.098716
BE	-0.31932	1	0.122897	-0.56605	-0.07259	1.121305
BG	0.522104	1	0.121419	0.278346	0.765862	1.097232
BH	0.364683	1	0.116435	0.130929	0.598437	1.088541
CD	0.449933	1	0.124822	0.199341	0.700524	1.159609
CH	-0.43049	1	0.117582	-0.66655	-0.19444	1.093345
DE	0.304832	1	0.127832	0.048198	0.561467	1.217225
DH	0.477266	1	0.120744	0.234863	0.719669	1.159725
EG	-0.45625	1	0.133029	-0.72332	-0.18918	1.295126
EH	-0.32154	1	0.121093	-0.56465	-0.07844	1.156879
EJ	0.304859	1	0.119613	0.064725	0.544993	1.12879
FJ	-0.32207	1	0.119582	-0.56214	-0.082	1.131747
GH	0.556687	1	0.116567	0.322668	0.790706	1.074564
GJ	-0.32944	1	0.119818	-0.56998	-0.08889	1.135328

Final Equation in Terms of Coded Factors:

Ln(Buildup =
-1.07018
-0.09837 * A
1.007999 * B
0.29226 * C
0.385746 * D
-0.35678 * E
0.095403 * F
-0.3271 * G
0.017392 * H
-0.42199 * J
0.351893 * A * E
-0.31932 * B * E
0.522104 * B * G
0.364683 * B * H
0.449933 * C * D
-0.43049 * C * H
0.304832 * D * E
0.477266 * D * H
-0.45625 * E * G
-0.32154 * E * H
0.304859 * E * J
-0.32207 * F * J
0.556687 * G * H
-0.32944 * G * J

Final Equation in Terms of Actual Factors:

Ln(Buildup =
50.38058
-0.15158 * Mass Polyester
0.208857 * Mass Styrene
-0.22421 * Mass LMA
-9.93376 * Mass DETA (Organic)
-0.05356 * Mass Water
0.069977 * Stirrer Speed
0.738337 * Initial Temperature
0.089807 * Acid Value
-0.0115 * Viscosity
0.000145 * Mass Polyester * Mass Water
-0.0003 * Mass Styrene * Mass Water
0.004012 * Mass Styrene * Initial Temperature
0.001813 * Mass Styrene * Acid Value
0.194178 * Mass LMA * Mass DETA (Organic)
-0.01361 * Mass LMA * Acid Value
0.005814 * Mass DETA (Organic) * Mass Water
0.048467 * Mass DETA (Organic) * Acid Value
-0.00099 * Mass Water * Initial Temperature
-0.00045 * Mass Water * Acid Value
2.51E-05 * Mass Water * Viscosity
-3.3E-05 * Stirrer Speed * Viscosity
0.006401 * Initial Temperature * Acid Value
-0.00022 * Initial Temperature * Viscosity

Response **1 Buildup**
Transform: Natural log Constant: 0.05
Stepwise Regression with Alpha to Enter = 0.100, Alpha to Exit = 0.100

Added	Coefficient Estimate	t for H0 Coeff=0	Prob > |t|	R-Squared	MSE
B-Mass St	0.94	-4.69	<0.0001	0.23	2.77
E-Mass W	-0.50	2.55	0.01	0.30	2.57
J-Viscosity	-0.42	2.34	0.02	0.35	2.42
GH	0.44	-2.39	0.02	0.40	2.27
D-Mass D	0.44	-2.49	0.02	0.45	2.11
BG	0.46	-2.57	0.01	0.49	1.96
G-Initial T	-0.41	2.50	0.01	0.54	1.82
DH	0.38	-2.34	0.02	0.57	1.70
EH	-0.33	2.06	0.04	0.60	1.62
CH	-0.32	2.11	0.04	0.63	1.54
C-Mass LM	0.32	-2.17	0.03	0.65	1.46
AE	0.29	-1.89	0.06	0.67	1.40
CD	0.29	-1.96	0.05	0.69	1.34
EG	-0.32	2.18	0.03	0.71	1.26
BH	0.30	-2.28	0.03	0.74	1.18
EJ	0.28	-2.11	0.04	0.75	1.11
FJ	-0.27	2.07	0.04	0.77	1.05
BE	-0.31	2.36	0.02	0.79	0.97
GJ	-0.27	2.26	0.03	0.81	0.91
DE	0.30	-2.41	0.02	0.83	0.83

Hierarchical Terms Added after StepWise Regression
A-Mass Polyester, F-Stirrer Speed, H-Acid Value

ANOVA for Response Surface Reduced 2FI Model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	219.1916	23	9.530069	11.09188	**< 0.0001**	significant
A-Mass Po	0.629018	1	0.629018	0.732103	0.3962	
B-Mass Sty	63.97659	1	63.97659	74.46121	**< 0.0001**	
C-Mass LM	5.386456	1	5.386456	6.2692	**0.0155**	
D-Mass DE	9.019256	1	9.019256	10.49735	**0.0021**	
E-Mass Wa	7.718523	1	7.718523	8.98345	**0.0042**	
F-Stirrer Sp	0.524516	1	0.524516	0.610474	0.4382	
G-Initial Te	6.745715	1	6.745715	7.851217	**0.0072**	
H-Acid Valu	0.019535	1	0.019535	0.022737	0.8807	
J-Viscosity	12.2884	1	12.2884	14.30225	**0.0004**	
AE	7.158903	1	7.158903	8.332119	**0.0057**	
BE	5.800442	1	5.800442	6.751031	**0.0122**	
BG	15.88669	1	15.88669	18.49023	**< 0.0001**	
BH	8.428533	1	8.428533	9.809819	**0.0029**	
CD	11.16352	1	11.16352	12.99302	**0.0007**	
CH	11.51702	1	11.51702	13.40445	**0.0006**	
DE	4.885755	1	4.885755	5.686443	**0.0209**	
DH	13.42402	1	13.42402	15.62397	**0.0002**	
EG	10.10661	1	10.10661	11.76291	**0.0012**	
EH	6.058113	1	6.058113	7.05093	**0.0105**	
EJ	5.581213	1	5.581213	6.495874	**0.0139**	
FJ	6.232448	1	6.232448	7.253835	**0.0096**	
GH	19.59559	1	19.59559	22.80695	**< 0.0001**	
GJ	6.495239	1	6.495239	7.559692	**0.0082**	
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Pure Error	0.078924	4	0.019731			
Cor Total	263.0105	74				

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Mean	-0.945	**Adj R-Squa**	0.758
C.V. %	98.116	**Pred R-Squ**	0.654
PRESS	91.054	**Adeq Preci**	11.601

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
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C-Mass LM	0.29226	1	0.116725	0.057925	0.526595	1.07493
D-Mass DE	0.385746	1	0.119059	0.146725	0.624766	1.136383
E-Mass Wa	-0.35678	1	0.119037	-0.59576	-0.11781	1.121462
F-Stirrer Sp	0.095403	1	0.122104	-0.14973	0.340537	1.176282
G-Initial Te	-0.3271	1	0.116739	-0.56147	-0.09274	1.077727
H-Acid Valu	0.017392	1	0.115344	-0.21417	0.248955	1.161133
J-Viscosity	-0.42199	1	0.111584	-0.64601	-0.19798	1.08667
AE	0.351893	1	0.121908	0.107152	0.596634	1.098716
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BG	0.522104	1	0.121419	0.278346	0.765862	1.097232
BH	0.364683	1	0.116435	0.130929	0.598437	1.088541
CD	0.449933	1	0.124822	0.199341	0.700524	1.159609
CH	-0.43049	1	0.117582	-0.66655	-0.19444	1.093345
DE	0.304832	1	0.127832	0.048198	0.561467	1.217225
DH	0.477266	1	0.120744	0.234863	0.719669	1.159725
EG	-0.45625	1	0.133029	-0.72332	-0.18918	1.295126
EH	-0.32154	1	0.121093	-0.56465	-0.07844	1.156879
EJ	0.304859	1	0.119613	0.064725	0.544993	1.12879
FJ	-0.32207	1	0.119582	-0.56214	-0.082	1.131747
GH	0.556687	1	0.116567	0.322668	0.790706	1.074564
GJ	-0.32944	1	0.119818	-0.56998	-0.08889	1.135328

Final Equation in Terms of Coded Factors:

Ln(Buildup =
-1.07018
-0.09837 * A
1.007999 * B
0.29226 * C
0.385746 * D
-0.35678 * E
0.095403 * F
-0.3271 * G
0.017392 * H
-0.42199 * J
0.351893 * A * E
-0.31932 * B * E
0.522104 * B * G
0.364683 * B * H
0.449933 * C * D
-0.43049 * C * H
0.304832 * D * E
0.477266 * D * H
-0.45625 * E * G
-0.32154 * E * H
0.304859 * E * J
-0.32207 * F * J
0.556687 * G * H
-0.32944 * G * J

Final Equation in Terms of Actual Factors:

Ln(Buildup =
50.38058
-0.15158 * Mass Polyester
0.208857 * Mass Styrene
-0.22421 * Mass LMA
-9.93376 * Mass DETA (Organic)
-0.05356 * Mass Water
0.069977 * Stirrer Speed
0.738337 * Initial Temperature
0.089807 * Acid Value
-0.0115 * Viscosity
0.000145 * Mass Polyester * Mass Water
-0.0003 * Mass Styrene * Mass Water
0.004012 * Mass Styrene * Initial Temperature
0.001813 * Mass Styrene * Acid Value
0.194178 * Mass LMA * Mass DETA (Organic)
-0.01361 * Mass LMA * Acid Value
0.005814 * Mass DETA (Organic) * Mass Water
0.048467 * Mass DETA (Organic) * Acid Value
-0.00099 * Mass Water * Initial Temperature
-0.00045 * Mass Water * Acid Value
2.51E-05 * Mass Water * Viscosity
-3.3E-05 * Stirrer Speed * Viscosity
0.006401 * Initial Temperature * Acid Value
-0.00022 * Initial Temperature * Viscosity

Appendix F.1 - Dimensional Analysis Data

Batch No:	σ /kg.s^{-2}	μ_c /kg.m^{-1}.s^{-1}	ρ_c /kg.m^{-3}	μ_d /kg.m^{-1}.s^{-1}	ρ_d /kg.m^{-3}	N /s^{-1}	D /m	d /m	α /m	(α / D)	Re	We	Fr	(ρ_c / ρ_d)	(μ_c / μ_d)		y	ym
SCR36-201	7.20E-04	0.0177	1001.9	0.3290	1079.3	5.85	0.063	0.112	5.07E-05	8.05E-04	76.17	12828	0.220	0.928	0.054	0.229	8.05E-04	7.20E-04
SCR36-202	8.30E-04	0.0188	1002.7	0.4360	1075.0	4.95	0.063	0.112	3.51E-05	5.57E-04	48.44	7935	0.157	0.933	0.043	0.245	5.57E-04	8.23E-04
SCR36-203	9.10E-04	0.0149	1001.2	0.1560	1074.0	5.00	0.063	0.112	2.51E-05	3.99E-04	136.63	7378	0.161	0.932	0.096	0.259	3.99E-04	5.98E-04
SCR36-204	9.60E-04	0.0166	1001.4	0.2770	1076.3	6.65	0.063	0.112	4.58E-05	7.27E-04	102.55	12397	0.284	0.930	0.060	0.221	7.27E-04	6.63E-04
SCR36-207	1.61E-03	0.0150	1003.5	0.0869	1079.7	5.03	0.063	0.112	3.51E-05	5.57E-04	248.21	4248	0.163	0.929	0.173	0.259	5.57E-04	5.60E-04
SCR36-208	9.90E-04	0.0181	1002.2	0.2060	1085.8	6.70	0.063	0.112	3.20E-05	5.07E-04	140.16	12311	0.288	0.923	0.088	0.248	5.07E-04	5.48E-04
SCR36-209	5.40E-04	0.0182	1004.5	0.1580	1084.3	5.80	0.063	0.112	2.51E-05	3.98E-04	157.98	16890	0.216	0.926	0.115	0.278	3.98E-04	4.31E-04
SCR36-214	1.72E-03	0.0184	1003.9	0.2885	1089.4	5.07	0.063	0.112	6.74E-05	1.07E-03	75.94	4066	0.165	0.922	0.064	0.263	1.07E-03	8.40E-04
SCR36-215	1.25E-03	0.0153	1002.9	0.5005	1091.3	5.03	0.063	0.112	7.77E-05	1.23E-03	43.56	5531	0.163	0.919	0.031	0.248	1.23E-03	1.12E-03
SCR36-218	9.20E-04	0.0191	1004.6	0.1630	1087.2	5.03	0.063	0.112	2.64E-05	4.18E-04	133.25	7486	0.163	0.924	0.117	0.244	4.18E-04	6.55E-04
SCR36-219	8.00E-04	0.0154	1004.4	0.2833	1078.0	5.00	0.063	0.112	6.04E-05	9.59E-04	75.51	8423	0.161	0.932	0.054	0.261	9.59E-04	7.01E-04
SCR36-221	1.02E-03	0.0108	1004.4	0.1130	1070.0	4.98	0.063	0.112	2.16E-05	3.43E-04	187.29	6514	0.159	0.939	0.096	0.273	3.43E-04	5.35E-04
SCR36-222	2.15E-03	0.0145	1002.2	0.2864	1096.8	6.63	0.063	0.112	6.62E-05	1.05E-03	100.82	5613	0.283	0.914	0.051	0.249	1.05E-03	8.49E-04
SCR36-223	7.70E-04	0.0154	1002.1	0.1110	1073.1	5.03	0.063	0.112	3.11E-05	4.94E-04	193.13	8828	0.163	0.934	0.139	0.268	4.94E-04	4.80E-04
SCR36-224	1.04E-03	0.0154	1001.8	0.2902	1070.7	5.02	0.063	0.112	6.46E-05	1.03E-03	73.46	6479	0.162	0.936	0.053	0.227	1.03E-03	8.38E-04
SCR36-225	9.70E-04	0.0166	1003.4	0.4260	1093.2	4.97	0.063	0.112	7.21E-05	1.14E-03	50.59	6952	0.158	0.918	0.039	0.223	1.14E-03	1.15E-03
SCR36-226	8.70E-04	0.0151	1003.7	0.1280	1071.1	6.77	0.063	0.112	2.81E-05	4.47E-04	224.74	14096	0.294	0.937	0.118	0.226	4.47E-04	4.61E-04
SCR36-227	7.50E-04	0.0190	1003.5	0.1282	1072.6	5.07	0.063	0.112	3.14E-05	4.98E-04	168.25	9180	0.165	0.936	0.148	0.241	4.98E-04	5.17E-04
SCR36-228	8.10E-04	0.0184	1003.6	0.3083	1078.0	4.97	0.063	0.112	4.38E-05	6.95E-04	68.93	8209	0.158	0.931	0.060	0.277	6.95E-04	6.42E-04
SCR36-229	9.40E-04	0.0202	1003.4	0.2577	1088.1	5.02	0.063	0.112	4.54E-05	7.21E-04	84.07	7284	0.162	0.922	0.078	0.264	7.21E-04	7.00E-04
SCR36-233	2.28E-03	0.0151	1003.8	0.2124	1083.9	6.68	0.063	0.112	6.11E-05	9.69E-04	135.37	5310	0.287	0.926	0.071	0.262	9.69E-04	6.24E-04
SCR36-234	6.90E-04	0.0150	1003.5	0.1320	1081.7	6.65	0.063	0.112	2.03E-05	3.23E-04	216.29	17335	0.284	0.928	0.114	0.260	3.23E-04	4.26E-04
SCR36-235	1.02E-03	0.0191	1001.7	0.0916	1077.5	5.07	0.063	0.112	3.30E-05	5.24E-04	236.68	6781	0.165	0.930	0.209	0.277	5.24E-04	4.41E-04
SCR36-237	1.18E-03	0.0184	1003.1	0.0868	1078.4	6.70	0.063	0.112	1.96E-05	3.11E-04	330.46	10258	0.288	0.930	0.212	0.259	3.11E-04	3.71E-04
SCR36-238	2.11E-03	0.0154	1003.2	0.1656	1089.8	5.02	0.063	0.112	4.96E-05	7.87E-04	131.03	3250	0.162	0.921	0.093	0.247	7.87E-04	8.46E-04
SCR36-239	4.80E-04	0.0188	1004.2	0.1227	1067.5	5.08	0.063	0.112	4.26E-05	6.75E-04	175.53	14370	0.166	0.941	0.153	0.243	6.75E-04	4.40E-04
SCR36-241	9.60E-04	0.0148	1004.8	0.1890	1076.7	6.70	0.063	0.112	2.08E-05	3.30E-04	151.49	12589	0.288	0.933	0.078	0.261	3.30E-04	4.76E-04
SCR36-242	3.50E-04	0.0153	1003.2	0.1293	1068.3	6.70	0.063	0.112	5.18E-05	8.22E-04	219.71	34261	0.288	0.939	0.118	0.229	8.22E-04	3.79E-04
SCR36-243	6.90E-04	0.0154	1001.2	0.3208	1092.8	5.85	0.063	0.112	5.86E-05	9.30E-04	79.09	13553	0.220	0.916	0.048	0.250	9.30E-04	7.63E-04
SCR36-244	6.10E-04	0.0178	1001.6	0.4255	1084.1	6.67	0.063	0.112	3.93E-05	6.23E-04	67.42	19751	0.285	0.924	0.042	0.232	6.23E-04	6.94E-04
SCR36-245	7.80E-04	0.0188	1004.2	0.2470	1074.1	6.63	0.063	0.112	2.13E-05	3.38E-04	114.49	15151	0.283	0.935	0.076	0.266	3.38E-04	4.48E-04
SCR36-246	5.30E-04	0.0153	1001.7	0.1190	1075.4	6.65	0.063	0.112	2.16E-05	3.42E-04	238.52	22437	0.284	0.931	0.129	0.260	3.42E-04	3.74E-04
SCR36-247	7.40E-04	0.0165	1001.4	0.1979	1082.1	5.82	0.063	0.112	4.82E-05	7.65E-04	126.23	12371	0.217	0.925	0.083	0.230	7.65E-04	6.48E-04
SCR36-249	2.40E-04	0.0147	1001.2	0.2347	1084.1	6.63	0.063	0.112	4.88E-05	7.74E-04	121.61	49699	0.283	0.924	0.063	0.217	7.74E-04	5.59E-04
SCR36-250	1.12E-03	0.0171	1004.7	0.1890	1095.6	6.70	0.063	0.112	2.65E-05	4.21E-04	154.15	10980	0.288	0.917	0.090	0.264	4.21E-04	5.50E-04
SCR36-251	1.42E-03	0.0147	1003.7	0.5770	1091.5	6.67	0.063	0.112	4.86E-05	7.71E-04	50.05	8542	0.285	0.920	0.025	0.248	7.71E-04	9.23E-04
SCR36-252	5.60E-04	0.0171	1001.9	0.1665	1079.5	6.73	0.063	0.112	2.97E-05	4.71E-04	173.27	21853	0.291	0.928	0.103	0.275	4.71E-04	3.88E-04
SCR36-253	9.90E-04	0.0153	1001.0	0.2970	1079.5	5.88	0.063	0.112	1.71E-05	2.71E-04	84.87	9437	0.222	0.927	0.052	0.247	2.71E-04	7.14E-04
SCR36-254	7.90E-04	0.0177	1002.9	0.2010	1079.9	6.65	0.063	0.112	1.92E-05	3.04E-04	141.80	15115	0.284	0.929	0.088	0.261	3.04E-04	4.67E-04
SCR36-256	1.00E-03	0.0149	1003.3	0.1650	1081.2	6.67	0.063	0.112	3.55E-05	5.63E-04	173.39	12016	0.285	0.928	0.090	0.214	5.63E-04	6.22E-04
SCR36-258	7.60E-04	0.0152	1003.7	0.2430	1090.5	5.85	0.063	0.112	3.33E-05	5.29E-04	104.20	12279	0.220	0.920	0.063	0.216	5.29E-04	8.14E-04
SCR36-273	9.90E-04	0.0159	1004.2	0.3420	1087.5	4.98	0.063	0.112	5.47E-05	8.68E-04	62.89	6821	0.159	0.923	0.046	0.250	8.68E-04	8.92E-04
SCR36-274	8.50E-04	0.0191	1004.0	0.6470	1097.2	6.65	0.063	0.112	4.83E-05	7.67E-04	44.76	14274	0.284	0.915	0.030	0.265	7.67E-04	7.79E-04
SCR36-275	7.80E-04	0.0212	1003.9	0.1003	1074.4	5.00	0.063	0.112	3.11E-05	4.93E-04	212.58	8611	0.161	0.934	0.211	0.227	4.93E-04	5.11E-04

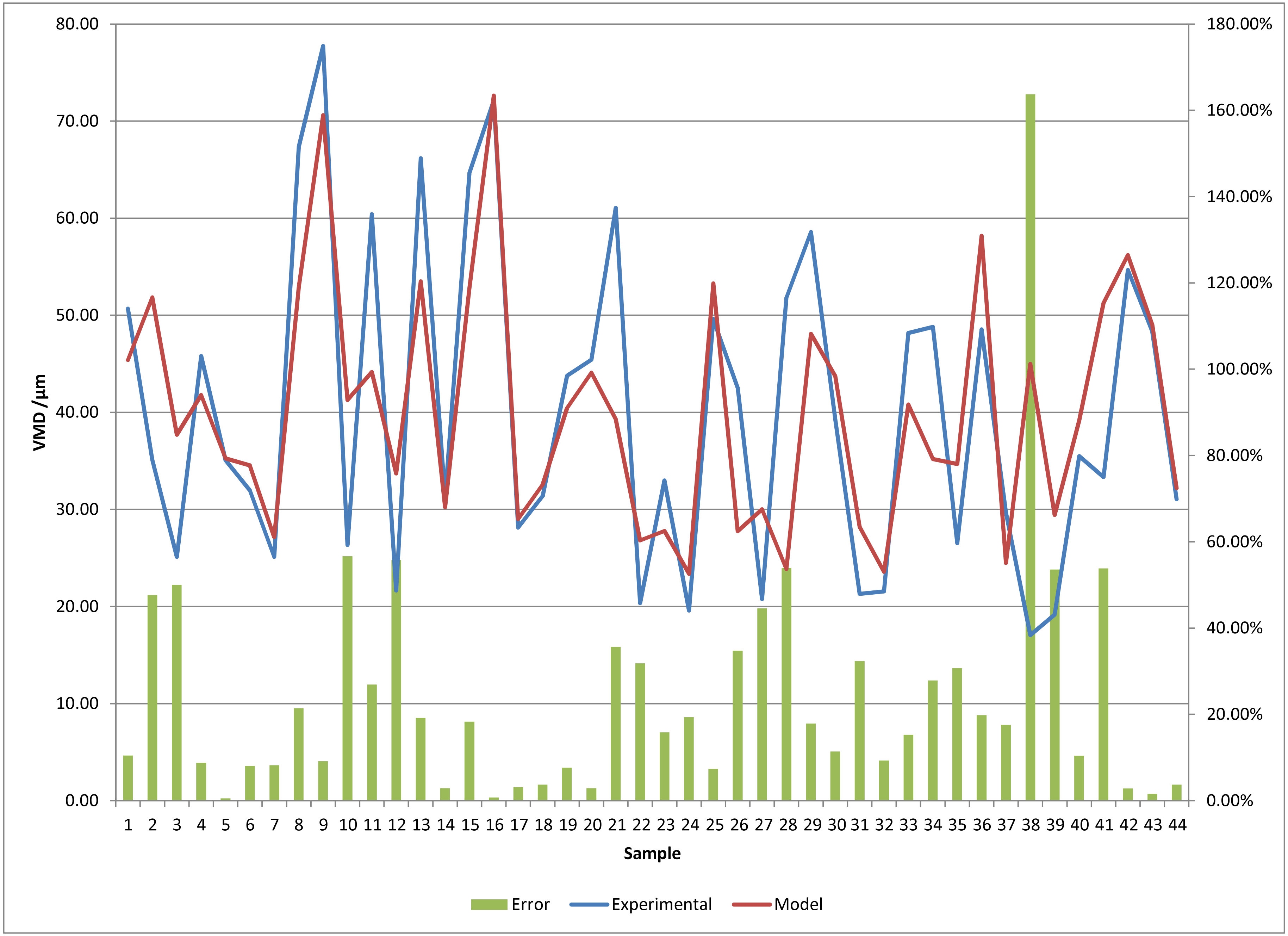
Batch No:	α /µm (experimental)	α /µm (model)	%Error	SS_{tot}	SS_{reg}	SS_{err}
SCR36-201	50.69	45.39	10.46%	111.758534	27.7518983	28.1280017
SCR36-202	35.11	51.85	47.69%	25.0841616	137.690761	280.313977
SCR36-203	25.12	37.69	50.04%	224.952275	5.89538172	158.014161
SCR36-204	45.80	41.78	8.78%	32.2804753	2.761379	16.1592033
SCR36-207	35.08	35.26	0.51%	25.3855662	23.5987804	0.03259884
SCR36-208	31.96	34.54	8.07%	66.5596389	31.1288791	6.65166938
SCR36-209	25.10	27.16	8.19%	225.552612	168.014308	4.22868134
SCR36-214	67.36	52.92	21.44%	742.104275	163.7858	208.620708
SCR36-215	77.74	70.61	9.18%	1415.3841	929.521674	50.8872933
SCR36-218	26.35	41.28	56.67%	189.569089	1.35287486	222.950904
SCR36-219	60.40	44.14	26.91%	411.34293	16.2059497	264.255244
SCR36-221	21.64	33.70	55.75%	341.451603	41.1434311	145.542377
SCR36-222	66.18	53.50	19.17%	679.206521	178.954105	160.889387
SCR36-223	31.12	30.23	2.86%	80.9713662	97.7782263	0.79188328
SCR36-224	64.64	52.82	18.28%	601.308421	161.351716	139.692576
SCR36-225	72.09	72.62	0.74%	1022.18263	1056.36388	0.28107076
SCR36-226	28.14	29.02	3.13%	143.482284	123.146796	0.77661301
SCR36-227	31.38	32.55	3.74%	76.3597934	57.2256259	1.37744723
SCR36-228	43.77	40.43	7.63%	13.3341162	0.09816627	11.1440863
SCR36-229	45.40	44.09	2.89%	27.8952025	15.7533442	1.72276818
SCR36-233	61.07	39.30	35.64%	438.969162	0.6657752	473.825858
SCR36-234	20.34	26.82	31.84%	391.185466	176.938319	41.9462533
SCR36-235	32.99	27.77	15.82%	50.8142162	152.473117	27.2441348
SCR36-237	19.58	23.36	19.33%	421.826248	280.681321	14.3251846
SCR36-238	49.61	53.28	7.40%	90.090298	173.24194	13.4729336
SCR36-239	42.55	27.75	34.78%	5.91263435	152.953619	219.011371
SCR36-241	20.76	30.02	44.59%	374.748003	102.056452	85.6755679
SCR36-242	51.80	23.87	53.93%	136.459566	264.113952	780.262208
SCR36-243	58.57	48.09	17.90%	340.461207	63.5000373	109.891189
SCR36-244	39.25	43.72	11.39%	0.75413435	12.9723957	19.982065
SCR36-245	21.30	28.19	32.36%	354.132521	142.218637	47.5115675
SCR36-246	21.56	23.57	9.32%	344.414548	273.900935	4.03389696
SCR36-247	48.17	40.81	15.28%	64.8281162	0.48044372	54.1467928
SCR36-249	48.79	35.19	27.87%	75.1964889	24.247805	184.845694
SCR36-250	26.52	34.68	30.76%	184.91673	29.6045295	66.5432504
SCR36-251	48.55	58.17	19.82%	71.0917253	326.028578	92.634283
SCR36-252	29.69	24.47	17.57%	108.751716	244.722536	27.1983214
SCR36-253	17.06	44.99	163.71%	531.69023	23.7160314	779.991053
SCR36-254	19.16	29.42	53.57%	439.254912	114.350005	105.369258
SCR36-256	35.48	39.17	10.41%	21.5148389	0.89509617	13.6331817
SCR36-258	33.32	51.26	53.83%	46.2183662	124.080188	321.755262
SCR36-273	54.67	56.21	2.81%	211.748798	258.903177	2.36814431
SCR36-274	48.30	49.05	1.56%	66.9384298	79.8408448	0.56818358
SCR36-275	31.05	32.20	3.70%	82.2360434	62.7415381	1.31664944
Average Error			**24.48%**	11310.32	6324.85025	5190.01296

Parameters	
k	**7.77E-05**
a	**-8.21E-04**
b	**-0.1856**
f	**-0.2979**
g	**-10.3941**
h	**-0.3314**
i	**-1.2176**

$$\left(\frac{\alpha}{D}\right) = kRe_d^{a}We_d^{b}Fr^{f}\left(\frac{\rho_c}{\rho_d}\right)^{g}\left(\frac{\mu_c}{\mu_d}\right)^{h}\phi^{i}$$

Dimensionless Model Equation 6.5

R^2	**0.5411259**


VMD /µm
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
180.00%
160.00%
140.00%
120.00%
100.00%
80.00%
60.00%
40.00%
20.00%
0.00%
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44
Sample
Error
Experimental
Model

Batch No:	σ /kg.s^{-2}	μ_c /kg.m^{-1}.s^{-1}	ρ_c /kg.m^{-3}	μ_d /kg.m^{-1}.s^{-1}	ρ_d /kg.m^{-3}	N /s^{-1}	D /m	d /m	α /m	(α / D)	Re	We	Fr	(ρ_c / ρ_d)	(μ_c / μ_d)		y	ym
SCR36-201	7.20E-04	0.0177	1001.9	0.3290	1079.3	5.85	0.063	0.112	5.07E-05	8.05E-04	76.17	12828	0.220	0.928	0.054	0.229	8.05E-04	2.91E-04
SCR36-202	8.30E-04	0.0188	1002.7	0.4360	1075.0	4.95	0.063	0.112	3.51E-05	5.57E-04	48.44	7935	0.157	0.933	0.043	0.245	5.57E-04	3.84E-04
SCR36-203	9.10E-04	0.0149	1001.2	0.1560	1074.0	5.00	0.063	0.112	2.51E-05	3.99E-04	136.63	7378	0.161	0.932	0.096	0.259	3.99E-04	6.41E-04
SCR36-204	9.60E-04	0.0166	1001.4	0.2770	1076.3	6.65	0.063	0.112	4.58E-05	7.27E-04	102.55	12397	0.284	0.930	0.060	0.221	7.27E-04	3.46E-04
SCR36-207	1.61E-03	0.0150	1003.5	0.0869	1079.7	5.03	0.063	0.112	3.51E-05	5.57E-04	248.21	4248	0.163	0.929	0.173	0.259	5.57E-04	1.41E-03
SCR36-208	9.90E-04	0.0181	1002.2	0.2060	1085.8	6.70	0.063	0.112	3.20E-05	5.07E-04	140.16	12311	0.288	0.923	0.088	0.248	5.07E-04	3.92E-04
SCR36-209	5.40E-04	0.0182	1004.5	0.1580	1084.3	5.80	0.063	0.112	2.51E-05	3.98E-04	157.98	16890	0.216	0.926	0.115	0.278	3.98E-04	2.95E-04
SCR36-214	1.72E-03	0.0184	1003.9	0.2885	1089.4	5.07	0.063	0.112	6.74E-05	1.07E-03	75.94	4066	0.165	0.922	0.064	0.263	1.07E-03	9.02E-04
SCR36-215	1.25E-03	0.0153	1002.9	0.5005	1091.3	5.03	0.063	0.112	7.77E-05	1.23E-03	43.56	5531	0.163	0.919	0.031	0.248	1.23E-03	5.41E-04
SCR36-218	9.20E-04	0.0191	1004.6	0.1630	1087.2	5.03	0.063	0.112	2.64E-05	4.18E-04	133.25	7486	0.163	0.924	0.117	0.244	4.18E-04	6.11E-04
SCR36-219	8.00E-04	0.0154	1004.4	0.2833	1078.0	5.00	0.063	0.112	6.04E-05	9.59E-04	75.51	8423	0.161	0.932	0.054	0.261	9.59E-04	4.41E-04
SCR36-221	1.02E-03	0.0108	1004.4	0.1130	1070.0	4.98	0.063	0.112	2.16E-05	3.43E-04	187.29	6514	0.159	0.939	0.096	0.273	3.43E-04	8.49E-04
SCR36-222	2.15E-03	0.0145	1002.2	0.2864	1096.8	6.63	0.063	0.112	6.62E-05	1.05E-03	100.82	5613	0.283	0.914	0.051	0.249	1.05E-03	7.71E-04
SCR36-223	7.70E-04	0.0154	1002.1	0.1110	1073.1	5.03	0.063	0.112	3.11E-05	4.94E-04	193.13	8828	0.163	0.934	0.139	0.268	4.94E-04	6.13E-04
SCR36-224	1.04E-03	0.0154	1001.8	0.2902	1070.7	5.02	0.063	0.112	6.46E-05	1.03E-03	73.46	6479	0.162	0.936	0.053	0.227	1.03E-03	5.67E-04
SCR36-225	9.70E-04	0.0166	1003.4	0.4260	1093.2	4.97	0.063	0.112	7.21E-05	1.14E-03	50.59	6952	0.158	0.918	0.039	0.223	1.14E-03	4.53E-04
SCR36-226	8.70E-04	0.0151	1003.7	0.1280	1071.1	6.77	0.063	0.112	2.81E-05	4.47E-04	224.74	14096	0.294	0.937	0.118	0.226	4.47E-04	4.21E-04
SCR36-227	7.50E-04	0.0190	1003.5	0.1282	1072.6	5.07	0.063	0.112	3.14E-05	4.98E-04	168.25	9180	0.165	0.936	0.148	0.241	4.98E-04	5.47E-04
SCR36-228	8.10E-04	0.0184	1003.6	0.3083	1078.0	4.97	0.063	0.112	4.38E-05	6.95E-04	68.93	8209	0.158	0.931	0.060	0.277	6.95E-04	4.29E-04
SCR36-229	9.40E-04	0.0202	1003.4	0.2577	1088.1	5.02	0.063	0.112	4.54E-05	7.21E-04	84.07	7284	0.162	0.922	0.078	0.264	7.21E-04	5.19E-04
SCR36-233	2.28E-03	0.0151	1003.8	0.2124	1083.9	6.68	0.063	0.112	6.11E-05	9.69E-04	135.37	5310	0.287	0.926	0.071	0.262	9.69E-04	9.13E-04
SCR36-234	6.90E-04	0.0150	1003.5	0.1320	1081.7	6.65	0.063	0.112	2.03E-05	3.23E-04	216.29	17335	0.284	0.928	0.114	0.260	3.23E-04	3.37E-04
SCR36-235	1.02E-03	0.0191	1001.7	0.0916	1077.5	5.07	0.063	0.112	3.30E-05	5.24E-04	236.68	6781	0.165	0.930	0.209	0.277	5.24E-04	8.48E-04
SCR36-237	1.18E-03	0.0184	1003.1	0.0868	1078.4	6.70	0.063	0.112	1.96E-05	3.11E-04	330.46	10258	0.288	0.930	0.212	0.259	3.11E-04	6.62E-04
SCR36-238	2.11E-03	0.0154	1003.2	0.1656	1089.8	5.02	0.063	0.112	4.96E-05	7.87E-04	131.03	3250	0.162	0.921	0.093	0.247	7.87E-04	1.43E-03
SCR36-239	4.80E-04	0.0188	1004.2	0.1227	1067.5	5.08	0.063	0.112	4.26E-05	6.75E-04	175.53	14370	0.166	0.941	0.153	0.243	6.75E-04	3.56E-04
SCR36-241	9.60E-04	0.0148	1004.8	0.1890	1076.7	6.70	0.063	0.112	2.08E-05	3.30E-04	151.49	12589	0.288	0.933	0.078	0.261	3.30E-04	4.03E-04
SCR36-242	3.50E-04	0.0153	1003.2	0.1293	1068.3	6.70	0.063	0.112	5.18E-05	8.22E-04	219.71	34261	0.288	0.939	0.118	0.229	8.22E-04	1.71E-04
SCR36-243	6.90E-04	0.0154	1001.2	0.3208	1092.8	5.85	0.063	0.112	5.86E-05	9.30E-04	79.09	13553	0.220	0.916	0.048	0.250	9.30E-04	2.84E-04
SCR36-244	6.10E-04	0.0178	1001.6	0.4255	1084.1	6.67	0.063	0.112	3.93E-05	6.23E-04	67.42	19751	0.285	0.924	0.042	0.232	6.23E-04	1.83E-04
SCR36-245	7.80E-04	0.0188	1004.2	0.2470	1074.1	6.63	0.063	0.112	2.13E-05	3.38E-04	114.49	15151	0.283	0.935	0.076	0.266	3.38E-04	2.92E-04
SCR36-246	5.30E-04	0.0153	1001.7	0.1190	1075.4	6.65	0.063	0.112	2.16E-05	3.42E-04	238.52	22437	0.284	0.931	0.129	0.260	3.42E-04	2.70E-04
SCR36-247	7.40E-04	0.0165	1001.4	0.1979	1082.1	5.82	0.063	0.112	4.82E-05	7.65E-04	126.23	12371	0.217	0.925	0.083	0.230	7.65E-04	3.72E-04
SCR36-249	2.40E-04	0.0147	1001.2	0.2347	1084.1	6.63	0.063	0.112	4.88E-05	7.74E-04	121.61	49699	0.283	0.924	0.063	0.217	7.74E-04	9.36E-05
SCR36-250	1.12E-03	0.0171	1004.7	0.1890	1095.6	6.70	0.063	0.112	2.65E-05	4.21E-04	154.15	10980	0.288	0.917	0.090	0.264	4.21E-04	4.60E-04
SCR36-251	1.42E-03	0.0147	1003.7	0.5770	1091.5	6.67	0.063	0.112	4.86E-05	7.71E-04	50.05	8542	0.285	0.920	0.025	0.248	7.71E-04	3.82E-04
SCR36-252	5.60E-04	0.0171	1001.9	0.1665	1079.5	6.73	0.063	0.112	2.97E-05	4.71E-04	173.27	21853	0.291	0.928	0.103	0.275	4.71E-04	2.42E-04
SCR36-253	9.90E-04	0.0153	1001.0	0.2970	1079.5	5.88	0.063	0.112	1.71E-05	2.71E-04	84.87	9437	0.222	0.927	0.052	0.247	2.71E-04	4.20E-04
SCR36-254	7.90E-04	0.0177	1002.9	0.2010	1079.9	6.65	0.063	0.112	1.92E-05	3.04E-04	141.80	15115	0.284	0.929	0.088	0.261	3.04E-04	3.21E-04
SCR36-256	1.00E-03	0.0149	1003.3	0.1650	1081.2	6.67	0.063	0.112	3.55E-05	5.63E-04	173.39	12016	0.285	0.928	0.090	0.214	5.63E-04	4.46E-04
SCR36-258	7.60E-04	0.0152	1003.7	0.2430	1090.5	5.85	0.063	0.112	3.33E-05	5.29E-04	104.20	12279	0.220	0.920	0.063	0.216	5.29E-04	3.51E-04
SCR36-273	9.90E-04	0.0159	1004.2	0.3420	1087.5	4.98	0.063	0.112	5.47E-05	8.68E-04	62.89	6821	0.159	0.923	0.046	0.250	8.68E-04	5.05E-04
SCR36-274	8.50E-04	0.0191	1004.0	0.6470	1097.2	6.65	0.063	0.112	4.83E-05	7.67E-04	44.76	14274	0.284	0.915	0.030	0.265	7.67E-04	2.13E-04
SCR36-275	7.80E-04	0.0212	1003.9	0.1003	1074.4	5.00	0.063	0.112	3.11E-05	4.93E-04	212.58	8611	0.161	0.934	0.211	0.227	4.93E-04	6.32E-04

Parameters	
K	0.31973

$$d_{p_{50}}/_D = KRe^{1/2}We^{-1}\left(\frac{\mu_d}{\mu_c}\right)^{0.1}$$

Dimensionless Model Equation 2.7

Hopff et. al. (1964)

α /µm (experimental)	α /µm (model)	%Error
50.69	18.36	63.79%
35.11	24.19	31.09%
25.12	40.36	60.67%
45.80	21.80	52.40%
35.08	89.05	153.84%
31.96	24.70	22.70%
25.10	18.61	25.87%
67.36	56.85	15.60%
77.74	34.07	56.18%
26.35	38.49	46.06%
60.40	27.80	53.97%
21.64	53.52	147.31%
66.18	48.56	26.62%
31.12	38.63	24.14%
64.64	35.74	44.71%
72.09	28.51	60.45%
28.14	26.53	5.73%
31.38	34.45	9.78%
43.77	27.01	38.30%
45.40	32.71	27.96%
61.07	57.49	5.85%
20.34	21.24	4.43%
32.99	53.45	62.03%
19.58	41.68	112.89%
49.61	89.96	81.33%
42.55	22.40	47.35%
20.76	25.41	22.38%
51.80	10.79	79.17%
58.57	17.91	69.43%
39.25	11.50	70.70%
21.30	18.40	13.60%
21.56	17.02	21.05%
48.17	23.45	51.31%
48.79	5.90	87.91%
26.52	28.96	9.21%
48.55	24.08	50.40%
29.69	15.23	48.69%
17.06	26.45	55.05%
19.16	20.23	5.60%
35.48	28.07	20.87%
33.32	22.09	33.69%
54.67	31.83	41.78%
48.30	13.43	72.20%
31.05	39.84	28.32%

Average Error	46.87%

y	ym
8.05E-04	6.93E-04
5.57E-04	9.53E-04
3.99E-04	6.23E-04
7.27E-04	6.17E-04
5.57E-04	5.57E-04
5.07E-04	5.40E-04
3.98E-04	4.71E-04
1.07E-03	9.36E-04
1.23E-03	1.10E-03
4.18E-04	6.26E-04
9.59E-04	7.77E-04
3.43E-04	5.64E-04
1.05E-03	7.65E-04
4.94E-04	5.12E-04
1.03E-03	8.42E-04
1.14E-03	9.70E-04
4.47E-04	4.26E-04
4.98E-04	5.37E-04
6.95E-04	8.12E-04
7.21E-04	7.68E-04
9.69E-04	6.84E-04
3.23E-04	4.10E-04
5.24E-04	5.02E-04
3.11E-04	3.91E-04
7.87E-04	7.86E-04
6.75E-04	4.69E-04
3.30E-04	5.20E-04
8.22E-04	3.41E-04
9.30E-04	6.73E-04
6.23E-04	6.53E-04
3.38E-04	5.57E-04
3.42E-04	3.67E-04
7.65E-04	5.63E-04
7.74E-04	3.99E-04
4.21E-04	5.34E-04
7.71E-04	9.27E-04
4.71E-04	4.24E-04
2.71E-04	7.18E-04
3.04E-04	5.09E-04
5.63E-04	4.96E-04
5.29E-04	6.14E-04
8.68E-04	8.88E-04
7.67E-04	8.48E-04
4.93E-04	4.93E-04

Parameters	
K	0.04928
a	-0.42
b	-0.2617
c	0.01058

$$\alpha/_D = KRe^{a}We^{b}\left(\frac{\mu_d}{\mu_c}\right)^{c}$$

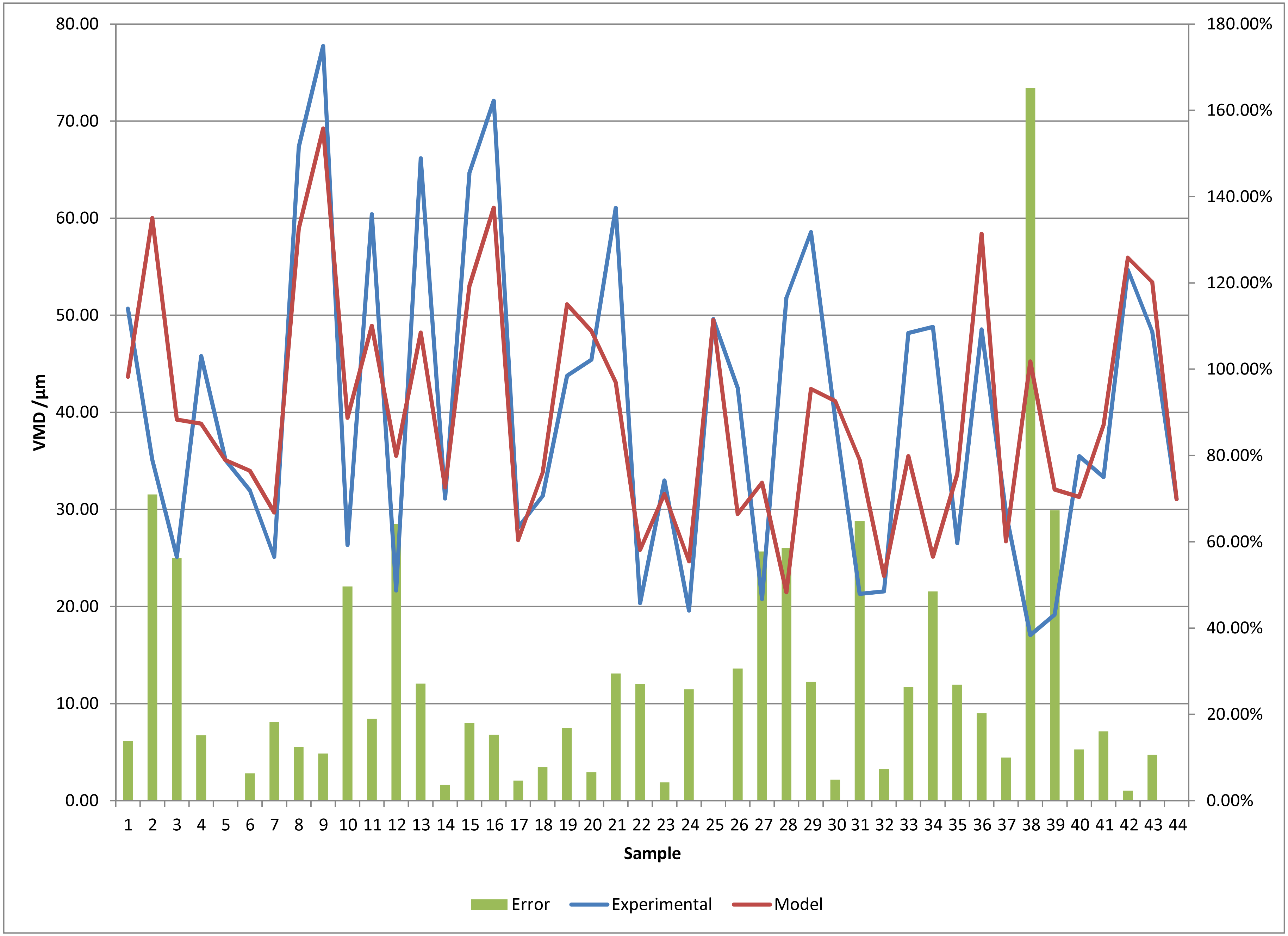
Dimensionless Model Equation 6.6

Hopff et. al. (1964)

α /µm (experimental)	α /µm (model)	%Error	SS_{tot}	SS_{reg}	SS_{err}
50.69	43.67	13.85%	111.758534	12.6194267	49.2692762
35.11	60.03	70.97%	25.0841616	396.311564	620.80629
25.12	39.25	56.25%	224.952275	0.75290946	199.676839
45.80	38.84	15.19%	32.2804753	1.6238273	48.3843463
35.08	35.07	0.02%	25.3855662	25.464343	6.1021E-05
31.96	33.99	6.36%	66.5596389	37.5279216	4.13067157
25.10	29.67	18.22%	225.552612	109.085724	20.9214571
67.36	58.96	12.47%	742.104275	354.952823	70.5835088
77.74	69.23	10.94%	1415.3841	847.735099	72.3469337
26.35	39.43	49.64%	189.569089	0.47508751	171.063986
60.40	48.92	19.00%	411.34293	77.5276295	131.712654
21.64	35.52	64.14%	341.451603	21.1463692	192.651373
66.18	48.22	27.13%	679.206521	65.6883144	322.445162
31.12	32.26	3.65%	80.9713662	61.8254639	1.28934227
64.64	53.02	17.97%	601.308421	166.575659	134.912211
72.09	61.09	15.26%	1022.18263	439.624627	121.096015
28.14	26.82	4.67%	143.482284	176.720309	1.72977736
31.38	33.81	7.74%	76.3597934	39.8227238	5.89462193
43.77	51.13	16.81%	13.3341162	121.221403	54.1470549
45.40	48.39	6.59%	27.8952025	68.4333126	8.94519601
61.07	43.08	29.46%	438.969162	8.77108784	323.639692
20.34	25.83	27.01%	391.185466	204.05022	30.1817758
32.99	31.60	4.23%	50.8142162	72.6342834	1.94369838
19.58	24.64	25.84%	421.826248	239.586624	25.6018098
49.61	49.52	0.19%	90.090298	88.3174777	0.00880839
42.55	29.53	30.61%	5.91263435	112.181183	169.602509
20.76	32.75	57.75%	374.748003	54.3092732	143.734359
51.80	21.46	58.56%	136.459566	347.969636	920.244694
58.57	42.42	27.57%	340.461207	5.3083777	260.744961
39.25	41.17	4.89%	0.75413435	1.10353631	3.68218664
21.30	35.10	64.81%	354.132521	25.1436564	190.552184
21.56	23.15	7.35%	344.414548	288.09049	2.51279711
48.17	35.49	26.31%	64.8281162	21.381285	160.670356
48.79	25.13	48.49%	75.1964889	224.550529	559.634773
26.52	33.64	26.86%	184.91673	41.9259627	50.7425855
48.55	58.40	20.29%	71.0917253	334.180493	97.0030644
29.69	26.72	10.02%	108.751716	179.61118	8.84170513
17.06	45.24	165.19%	531.69023	26.243444	794.182549
19.16	32.06	67.31%	439.254912	64.9820759	166.339393
35.48	31.28	11.85%	21.5148389	78.1750558	17.6673677
33.32	38.67	16.04%	46.2183662	2.11065236	28.5754463
54.67	55.92	2.29%	211.748798	249.682694	1.56190033
48.30	53.43	10.62%	66.9384298	177.175812	26.3081753
31.05	31.05	0.01%	82.2360434	82.3010678	1.2849E-05

Average Error		26.83%	11310.32	5954.92063	6215.98358

R^2	0.4504149



VMD /µm
Sample
Error
Experimental
Model

Batch No:	σ /kg.s^{-2}	μ_c /kg.m^{-1}.s^{-1}	ρ_c /kg.m^{-3}	μ_d /kg.m^{-1}.s^{-1}	ρ_d /kg.m^{-3}	N /s^{-1}	D /m	d /m	α /m	(α / D)	Re	We	Fr	(ρ_c / ρ_d)	(μ_c / μ_d)		y	ym
SCR36-201	7.20E-04	0.0177	1001.9	0.3290	1079.3	5.85	0.063	0.112	5.07E-05	8.05E-04	76.17	12828	0.220	0.928	0.054	0.229	8.05E-04	6.51E-04
SCR36-202	8.30E-04	0.0188	1002.7	0.4360	1075.0	4.95	0.063	0.112	3.51E-05	5.57E-04	48.44	7935	0.157	0.933	0.043	0.245	5.57E-04	7.71E-04
SCR36-203	9.10E-04	0.0149	1001.2	0.1560	1074.0	5.00	0.063	0.112	2.51E-05	3.99E-04	136.63	7378	0.161	0.932	0.096	0.259	3.99E-04	6.44E-04
SCR36-204	9.60E-04	0.0166	1001.4	0.2770	1076.3	6.65	0.063	0.112	4.58E-05	7.27E-04	102.55	12397	0.284	0.930	0.060	0.221	7.27E-04	5.63E-04
SCR36-207	1.61E-03	0.0150	1003.5	0.0869	1079.7	5.03	0.063	0.112	3.51E-05	5.57E-04	248.21	4248	0.163	0.929	0.173	0.259	5.57E-04	6.43E-04
SCR36-208	9.90E-04	0.0181	1002.2	0.2060	1085.8	6.70	0.063	0.112	3.20E-05	5.07E-04	140.16	12311	0.288	0.923	0.088	0.248	5.07E-04	5.98E-04
SCR36-209	5.40E-04	0.0182	1004.5	0.1580	1084.3	5.80	0.063	0.112	2.51E-05	3.98E-04	157.98	16890	0.216	0.926	0.115	0.278	3.98E-04	6.67E-04
SCR36-214	1.72E-03	0.0184	1003.9	0.2885	1089.4	5.07	0.063	0.112	6.74E-05	1.07E-03	75.94	4066	0.165	0.922	0.064	0.263	1.07E-03	7.45E-04
SCR36-215	1.25E-03	0.0153	1002.9	0.5005	1091.3	5.03	0.063	0.112	7.77E-05	1.23E-03	43.56	5531	0.163	0.919	0.031	0.248	1.23E-03	6.52E-04
SCR36-218	9.20E-04	0.0191	1004.6	0.1630	1087.2	5.03	0.063	0.112	2.64E-05	4.18E-04	133.25	7486	0.163	0.924	0.117	0.244	4.18E-04	7.70E-04
SCR36-219	8.00E-04	0.0154	1004.4	0.2833	1078.0	5.00	0.063	0.112	6.04E-05	9.59E-04	75.51	8423	0.161	0.932	0.054	0.261	9.59E-04	6.58E-04
SCR36-221	1.02E-03	0.0108	1004.4	0.1130	1070.0	4.98	0.063	0.112	2.16E-05	3.43E-04	187.29	6514	0.159	0.939	0.096	0.273	3.43E-04	5.06E-04
SCR36-222	2.15E-03	0.0145	1002.2	0.2864	1096.8	6.63	0.063	0.112	6.62E-05	1.05E-03	100.82	5613	0.283	0.914	0.051	0.249	1.05E-03	5.10E-04
SCR36-223	7.70E-04	0.0154	1002.1	0.1110	1073.1	5.03	0.063	0.112	3.11E-05	4.94E-04	193.13	8828	0.163	0.934	0.139	0.268	4.94E-04	6.56E-04
SCR36-224	1.04E-03	0.0154	1001.8	0.2902	1070.7	5.02	0.063	0.112	6.46E-05	1.03E-03	73.46	6479	0.162	0.936	0.053	0.227	1.03E-03	6.58E-04
SCR36-225	9.70E-04	0.0166	1003.4	0.4260	1093.2	4.97	0.063	0.112	7.21E-05	1.14E-03	50.59	6952	0.158	0.918	0.039	0.223	1.14E-03	7.00E-04
SCR36-226	8.70E-04	0.0151	1003.7	0.1280	1071.1	6.77	0.063	0.112	2.81E-05	4.47E-04	224.74	14096	0.294	0.937	0.118	0.226	4.47E-04	5.17E-04
SCR36-227	7.50E-04	0.0190	1003.5	0.1282	1072.6	5.07	0.063	0.112	3.14E-05	4.98E-04	168.25	9180	0.165	0.936	0.148	0.241	4.98E-04	7.63E-04
SCR36-228	8.10E-04	0.0184	1003.6	0.3083	1078.0	4.97	0.063	0.112	4.38E-05	6.95E-04	68.93	8209	0.158	0.931	0.060	0.277	6.95E-04	7.56E-04
SCR36-229	9.40E-04	0.0202	1003.4	0.2577	1088.1	5.02	0.063	0.112	4.54E-05	7.21E-04	84.07	7284	0.162	0.922	0.078	0.264	7.21E-04	8.05E-04
SCR36-233	2.28E-03	0.0151	1003.8	0.2124	1083.9	6.68	0.063	0.112	6.11E-05	9.69E-04	135.37	5310	0.287	0.926	0.071	0.262	9.69E-04	5.22E-04
SCR36-234	6.90E-04	0.0150	1003.5	0.1320	1081.7	6.65	0.063	0.112	2.03E-05	3.23E-04	216.29	17335	0.284	0.928	0.114	0.260	3.23E-04	5.21E-04
SCR36-235	1.02E-03	0.0191	1001.7	0.0916	1077.5	5.07	0.063	0.112	3.30E-05	5.24E-04	236.68	6781	0.165	0.930	0.209	0.277	5.24E-04	7.67E-04
SCR36-237	1.18E-03	0.0184	1003.1	0.0868	1078.4	6.70	0.063	0.112	1.96E-05	3.11E-04	330.46	10258	0.288	0.930	0.212	0.259	3.11E-04	6.05E-04
SCR36-238	2.11E-03	0.0154	1003.2	0.1656	1089.8	5.02	0.063	0.112	4.96E-05	7.87E-04	131.03	3250	0.162	0.921	0.093	0.247	7.87E-04	6.57E-04
SCR36-239	4.80E-04	0.0188	1004.2	0.1227	1067.5	5.08	0.063	0.112	4.26E-05	6.75E-04	175.53	14370	0.166	0.941	0.153	0.243	6.75E-04	7.55E-04
SCR36-241	9.60E-04	0.0148	1004.8	0.1890	1076.7	6.70	0.063	0.112	2.08E-05	3.30E-04	151.49	12589	0.288	0.933	0.078	0.261	3.30E-04	5.13E-04
SCR36-242	3.50E-04	0.0153	1003.2	0.1293	1068.3	6.70	0.063	0.112	5.18E-05	8.22E-04	219.71	34261	0.288	0.939	0.118	0.229	8.22E-04	5.26E-04
SCR36-243	6.90E-04	0.0154	1001.2	0.3208	1092.8	5.85	0.063	0.112	5.86E-05	9.30E-04	79.09	13553	0.220	0.916	0.048	0.250	9.30E-04	5.86E-04
SCR36-244	6.10E-04	0.0178	1001.6	0.4255	1084.1	6.67	0.063	0.112	3.93E-05	6.23E-04	67.42	19751	0.285	0.924	0.042	0.232	6.23E-04	5.93E-04
SCR36-245	7.80E-04	0.0188	1004.2	0.2470	1074.1	6.63	0.063	0.112	2.13E-05	3.38E-04	114.49	15151	0.283	0.935	0.076	0.266	3.38E-04	6.18E-04
SCR36-246	5.30E-04	0.0153	1001.7	0.1190	1075.4	6.65	0.063	0.112	2.16E-05	3.42E-04	238.52	22437	0.284	0.931	0.129	0.260	3.42E-04	5.30E-04
SCR36-247	7.40E-04	0.0165	1001.4	0.1979	1082.1	5.82	0.063	0.112	4.82E-05	7.65E-04	126.23	12371	0.217	0.925	0.083	0.230	7.65E-04	6.20E-04
SCR36-249	2.40E-04	0.0147	1001.2	0.2347	1084.1	6.63	0.063	0.112	4.88E-05	7.74E-04	121.61	49699	0.283	0.924	0.063	0.217	7.74E-04	5.15E-04
SCR36-250	1.12E-03	0.0171	1004.7	0.1890	1095.6	6.70	0.063	0.112	2.65E-05	4.21E-04	154.15	10980	0.288	0.917	0.090	0.264	4.21E-04	5.72E-04
SCR36-251	1.42E-03	0.0147	1003.7	0.5770	1091.5	6.67	0.063	0.112	4.86E-05	7.71E-04	50.05	8542	0.285	0.920	0.025	0.248	7.71E-04	5.13E-04
SCR36-252	5.60E-04	0.0171	1001.9	0.1665	1079.5	6.73	0.063	0.112	2.97E-05	4.71E-04	173.27	21853	0.291	0.928	0.103	0.275	4.71E-04	5.71E-04
SCR36-253	9.90E-04	0.0153	1001.0	0.2970	1079.5	5.88	0.063	0.112	1.71E-05	2.71E-04	84.87	9437	0.222	0.927	0.052	0.247	2.71E-04	5.81E-04
SCR36-254	7.90E-04	0.0177	1002.9	0.2010	1079.9	6.65	0.063	0.112	1.92E-05	3.04E-04	141.80	15115	0.284	0.929	0.088	0.261	3.04E-04	5.91E-04
SCR36-256	1.00E-03	0.0149	1003.3	0.1650	1081.2	6.67	0.063	0.112	3.55E-05	5.63E-04	173.39	12016	0.285	0.928	0.090	0.214	5.63E-04	5.18E-04
SCR36-258	7.60E-04	0.0152	1003.7	0.2430	1090.5	5.85	0.063	0.112	3.33E-05	5.29E-04	104.20	12279	0.220	0.920	0.063	0.216	5.29E-04	5.80E-04
SCR36-273	9.90E-04	0.0159	1004.2	0.3420	1087.5	4.98	0.063	0.112	5.47E-05	8.68E-04	62.89	6821	0.159	0.923	0.046	0.250	8.68E-04	6.76E-04
SCR36-274	8.50E-04	0.0191	1004.0	0.6470	1097.2	6.65	0.063	0.112	4.83E-05	7.67E-04	44.76	14274	0.284	0.915	0.030	0.265	7.67E-04	6.25E-04
SCR36-275	7.80E-04	0.0212	1003.9	0.1003	1074.4	5.00	0.063	0.112	3.11E-05	4.93E-04	212.58	8611	0.161	0.934	0.211	0.227	4.93E-04	8.37E-04

Parameters

K	2.6773

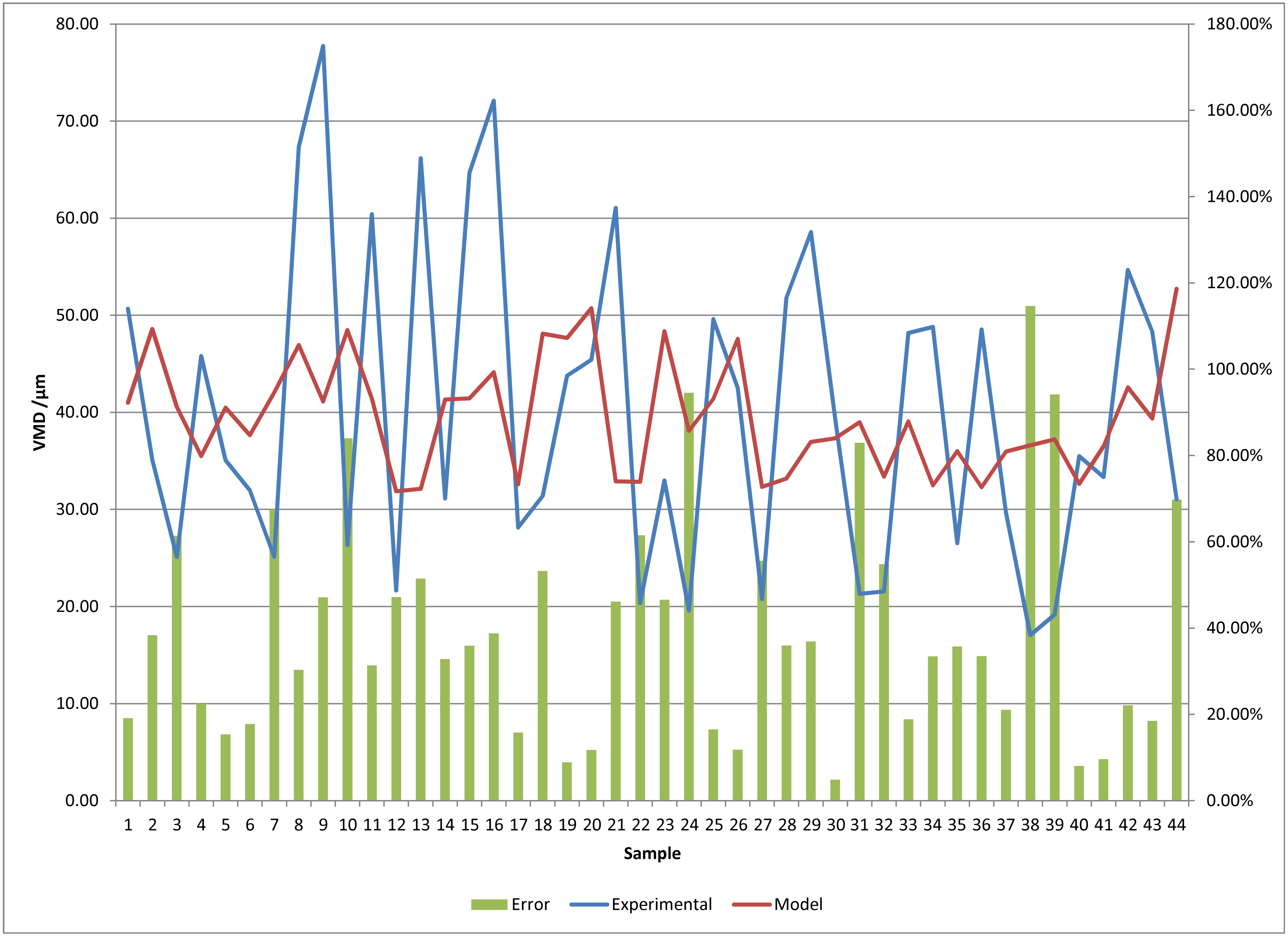
$$d_{p_{max}}/_{D} = K\left(\frac{\rho_c N d^2}{\mu D}\right)^{-0.75}$$

Model Equation 2.8

Arai et. al. (1977)

Batch No:	α /μm (experimental)	α /μm (model)	%Error	SS_{tot}	SS_{reg}	SS_{err}
SCR36-201	50.69	40.99	19.13%	111.758534	0.76507945	94.0299221
SCR36-202	35.11	48.58	38.38%	25.0841616	71.6831332	181.57558
SCR36-203	25.12	40.55	61.42%	224.952275	0.18600278	238.075318
SCR36-204	45.80	35.50	22.49%	32.2804753	21.3321533	106.095466
SCR36-207	35.08	40.48	15.40%	25.3855662	0.13170043	29.1741997
SCR36-208	31.96	37.64	17.79%	66.5596389	6.11959889	32.3149817
SCR36-209	25.10	42.05	67.52%	225.552612	3.71985153	287.204224
SCR36-214	67.36	46.94	30.32%	742.104275	46.4996881	417.079443
SCR36-215	77.74	41.11	47.12%	1415.3841	0.97427568	1342.08929
SCR36-218	26.35	48.48	84.00%	189.569089	69.9941295	489.943108
SCR36-219	60.40	41.47	31.35%	411.34293	1.81775968	358.471656
SCR36-221	21.64	31.86	47.22%	341.451603	68.2400632	104.400468
SCR36-222	66.18	32.12	51.47%	679.206521	64.0316242	1160.32661
SCR36-223	31.12	41.33	32.81%	80.9713662	1.47165263	104.275263
SCR36-224	64.64	41.44	35.89%	601.308421	1.7565934	538.064879
SCR36-225	72.09	44.12	38.80%	1022.18263	16.0185802	782.280011
SCR36-226	28.14	32.58	15.78%	143.482284	56.8122693	19.722638
SCR36-227	31.38	48.10	53.27%	76.3597934	63.6285725	279.39661
SCR36-228	43.77	47.66	8.88%	13.3341162	56.8028641	15.094597
SCR36-229	45.40	50.74	11.75%	27.8952025	112.723963	28.4682353
SCR36-233	61.07	32.88	46.16%	438.969162	52.3544226	794.519739
SCR36-234	20.34	32.85	61.50%	391.185466	52.8355223	156.490201
SCR36-235	32.99	48.35	46.56%	50.8142162	67.7581859	235.927915
SCR36-237	19.58	38.09	94.51%	421.826248	4.13079548	342.471046
SCR36-238	49.61	41.40	16.55%	90.090298	1.64347441	67.3977005
SCR36-239	42.55	47.57	11.80%	5.91263435	55.566367	25.2274574
SCR36-241	20.76	32.31	55.62%	374.748003	61.0183461	133.332863
SCR36-242	51.80	33.16	35.98%	136.459566	48.3947306	347.383358
SCR36-243	58.57	36.95	36.92%	340.461207	10.0471565	467.481301
SCR36-244	39.25	37.33	4.89%	0.75413435	7.76531279	3.67957561
SCR36-245	21.30	38.96	82.93%	354.132521	1.33125447	312.038414
SCR36-246	21.56	33.39	54.85%	344.414548	45.3246487	139.855477
SCR36-247	48.17	39.07	18.89%	64.8281162	1.09460322	82.7703976
SCR36-249	48.79	32.47	33.44%	75.1964889	58.4613617	266.263871
SCR36-250	26.52	36.01	35.77%	184.91673	16.9086578	89.991695
SCR36-251	48.55	32.29	33.49%	71.0917253	61.2823327	264.38416
SCR36-252	29.69	35.95	21.08%	108.751716	17.3940747	39.159919
SCR36-253	17.06	36.62	114.64%	531.69023	12.2547711	382.504708
SCR36-254	19.16	37.21	94.20%	439.254912	8.47041558	325.73071
SCR36-256	35.48	32.63	8.04%	21.5148389	56.0943568	8.12938426
SCR36-258	33.32	36.52	9.60%	46.2183662	12.9497312	10.2389479
SCR36-273	54.67	42.59	22.10%	211.748798	6.08505802	146.042388
SCR36-274	48.30	39.36	18.51%	66.9384298	0.57252287	79.8921936
SCR36-275	31.05	52.72	69.79%	82.2360434	158.791269	469.573726
Average Error			**39.97%**	11310.32	1483.23893	11798.5696

R^2	**-0.0431685**



80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
VMD /µm
180.00%
160.00%
140.00%
120.00%
100.00%
80.00%
60.00%
40.00%
20.00%
0.00%
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44
Sample
Error
Experimental
Model

Batch No:	σ /kg.s^{-2}	μ_c /kg.m^{-1}.s^{-1}	ρ_c /kg.m^{-3}	μ_d /kg.m^{-1}.s^{-1}	ρ_d /kg.m^{-3}	N /s^{-1}	D /m	d /m	α /m	(α / D)	Re	We	Fr	(ρ_c / ρ_d)	(μ_c / μ_d)		y	ym
SCR36-201	7.20E-04	0.0177	1001.9	0.3290	1079.3	5.85	0.063	0.112	5.07E-05	8.05E-04	76.17	12828	0.220	0.928	0.054	0.229	8.05E-04	7.24E-04
SCR36-202	8.30E-04	0.0188	1002.7	0.4360	1075.0	4.95	0.063	0.112	3.51E-05	5.57E-04	48.44	7935	0.157	0.933	0.043	0.245	5.57E-04	5.61E-04
SCR36-203	9.10E-04	0.0149	1001.2	0.1560	1074.0	5.00	0.063	0.112	2.51E-05	3.99E-04	136.63	7378	0.161	0.932	0.096	0.259	3.99E-04	4.90E-04
SCR36-204	9.60E-04	0.0166	1001.4	0.2770	1076.3	6.65	0.063	0.112	4.58E-05	7.27E-04	102.55	12397	0.284	0.930	0.060	0.221	7.27E-04	7.60E-04
SCR36-207	1.61E-03	0.0150	1003.5	0.0869	1079.7	5.03	0.063	0.112	3.51E-05	5.57E-04	248.21	4248	0.163	0.929	0.173	0.259	5.57E-04	4.16E-04
SCR36-208	9.90E-04	0.0181	1002.2	0.2060	1085.8	6.70	0.063	0.112	3.20E-05	5.07E-04	140.16	12311	0.288	0.923	0.088	0.248	5.07E-04	6.23E-04
SCR36-209	5.40E-04	0.0182	1004.5	0.1580	1084.3	5.80	0.063	0.112	2.51E-05	3.98E-04	157.98	16890	0.216	0.926	0.115	0.278	3.98E-04	5.21E-04
SCR36-214	1.72E-03	0.0184	1003.9	0.2885	1089.4	5.07	0.063	0.112	6.74E-05	1.07E-03	75.94	4066	0.165	0.922	0.064	0.263	1.07E-03	3.97E-04
SCR36-215	1.25E-03	0.0153	1002.9	0.5005	1091.3	5.03	0.063	0.112	7.77E-05	1.23E-03	43.56	5531	0.163	0.919	0.031	0.248	1.23E-03	4.91E-04
SCR36-218	9.20E-04	0.0191	1004.6	0.1630	1087.2	5.03	0.063	0.112	2.64E-05	4.18E-04	133.25	7486	0.163	0.924	0.117	0.244	4.18E-04	5.56E-04
SCR36-219	8.00E-04	0.0154	1004.4	0.2833	1078.0	5.00	0.063	0.112	6.04E-05	9.59E-04	75.51	8423	0.161	0.932	0.054	0.261	9.59E-04	5.00E-04
SCR36-221	1.02E-03	0.0108	1004.4	0.1130	1070.0	4.98	0.063	0.112	2.16E-05	3.43E-04	187.29	6514	0.159	0.939	0.096	0.273	3.43E-04	4.15E-04
SCR36-222	2.15E-03	0.0145	1002.2	0.2864	1096.8	6.63	0.063	0.112	6.62E-05	1.05E-03	100.82	5613	0.283	0.914	0.051	0.249	1.05E-03	4.92E-04
SCR36-223	7.70E-04	0.0154	1002.1	0.1110	1073.1	5.03	0.063	0.112	3.11E-05	4.94E-04	193.13	8828	0.163	0.934	0.139	0.268	4.94E-04	4.77E-04
SCR36-224	1.04E-03	0.0154	1001.8	0.2902	1070.7	5.02	0.063	0.112	6.46E-05	1.03E-03	73.46	6479	0.162	0.936	0.053	0.227	1.03E-03	6.00E-04
SCR36-225	9.70E-04	0.0166	1003.4	0.4260	1093.2	4.97	0.063	0.112	7.21E-05	1.14E-03	50.59	6952	0.158	0.918	0.039	0.223	1.14E-03	6.30E-04
SCR36-226	8.70E-04	0.0151	1003.7	0.1280	1071.1	6.77	0.063	0.112	2.81E-05	4.47E-04	224.74	14096	0.294	0.937	0.118	0.226	4.47E-04	7.60E-04
SCR36-227	7.50E-04	0.0190	1003.5	0.1282	1072.6	5.07	0.063	0.112	3.14E-05	4.98E-04	168.25	9180	0.165	0.936	0.148	0.241	4.98E-04	6.01E-04
SCR36-228	8.10E-04	0.0184	1003.6	0.3083	1078.0	4.97	0.063	0.112	4.38E-05	6.95E-04	68.93	8209	0.158	0.931	0.060	0.277	6.95E-04	4.25E-04
SCR36-229	9.40E-04	0.0202	1003.4	0.2577	1088.1	5.02	0.063	0.112	4.54E-05	7.21E-04	84.07	7284	0.162	0.922	0.078	0.264	7.21E-04	4.68E-04
SCR36-233	2.28E-03	0.0151	1003.8	0.2124	1083.9	6.68	0.063	0.112	6.11E-05	9.69E-04	135.37	5310	0.287	0.926	0.071	0.262	9.69E-04	4.34E-04
SCR36-234	6.90E-04	0.0150	1003.5	0.1320	1081.7	6.65	0.063	0.112	2.03E-05	3.23E-04	216.29	17335	0.284	0.928	0.114	0.260	3.23E-04	6.26E-04
SCR36-235	1.02E-03	0.0191	1001.7	0.0916	1077.5	5.07	0.063	0.112	3.30E-05	5.24E-04	236.68	6781	0.165	0.930	0.209	0.277	5.24E-04	4.03E-04
SCR36-237	1.18E-03	0.0184	1003.1	0.0868	1078.4	6.70	0.063	0.112	1.96E-05	3.11E-04	330.46	10258	0.288	0.930	0.212	0.259	3.11E-04	5.40E-04
SCR36-238	2.11E-03	0.0154	1003.2	0.1656	1089.8	5.02	0.063	0.112	4.96E-05	7.87E-04	131.03	3250	0.162	0.921	0.093	0.247	7.87E-04	4.23E-04
SCR36-239	4.80E-04	0.0188	1004.2	0.1227	1067.5	5.08	0.063	0.112	4.26E-05	6.75E-04	175.53	14370	0.166	0.941	0.153	0.243	6.75E-04	6.80E-04
SCR36-241	9.60E-04	0.0148	1004.8	0.1890	1076.7	6.70	0.063	0.112	2.08E-05	3.30E-04	151.49	12589	0.288	0.933	0.078	0.261	3.30E-04	5.65E-04
SCR36-242	3.50E-04	0.0153	1003.2	0.1293	1068.3	6.70	0.063	0.112	5.18E-05	8.22E-04	219.71	34261	0.288	0.939	0.118	0.229	8.22E-04	9.72E-04
SCR36-243	6.90E-04	0.0154	1001.2	0.3208	1092.8	5.85	0.063	0.112	5.86E-05	9.30E-04	79.09	13553	0.220	0.916	0.048	0.250	9.30E-04	6.30E-04
SCR36-244	6.10E-04	0.0178	1001.6	0.4255	1084.1	6.67	0.063	0.112	3.93E-05	6.23E-04	67.42	19751	0.285	0.924	0.042	0.232	6.23E-04	8.10E-04
SCR36-245	7.80E-04	0.0188	1004.2	0.2470	1074.1	6.63	0.063	0.112	2.13E-05	3.38E-04	114.49	15151	0.283	0.935	0.076	0.266	3.38E-04	5.68E-04
SCR36-246	5.30E-04	0.0153	1001.7	0.1190	1075.4	6.65	0.063	0.112	2.16E-05	3.42E-04	238.52	22437	0.284	0.931	0.129	0.260	3.42E-04	6.78E-04
SCR36-247	7.40E-04	0.0165	1001.4	0.1979	1082.1	5.82	0.063	0.112	4.82E-05	7.65E-04	126.23	12371	0.217	0.925	0.083	0.230	7.65E-04	7.14E-04
SCR36-249	2.40E-04	0.0147	1001.2	0.2347	1084.1	6.63	0.063	0.112	4.88E-05	7.74E-04	121.61	49699	0.283	0.924	0.063	0.217	7.74E-04	1.18E-03
SCR36-250	1.12E-03	0.0171	1004.7	0.1890	1095.6	6.70	0.063	0.112	2.65E-05	4.21E-04	154.15	10980	0.288	0.917	0.090	0.264	4.21E-04	5.27E-04
SCR36-251	1.42E-03	0.0147	1003.7	0.5770	1091.5	6.67	0.063	0.112	4.86E-05	7.71E-04	50.05	8542	0.285	0.920	0.025	0.248	7.71E-04	5.59E-04
SCR36-252	5.60E-04	0.0171	1001.9	0.1665	1079.5	6.73	0.063	0.112	2.97E-05	4.71E-04	173.27	21853	0.291	0.928	0.103	0.275	4.71E-04	5.81E-04
SCR36-253	9.90E-04	0.0153	1001.0	0.2970	1079.5	5.88	0.063	0.112	1.71E-05	2.71E-04	84.87	9437	0.222	0.927	0.052	0.247	2.71E-04	5.83E-04
SCR36-254	7.90E-04	0.0177	1002.9	0.2010	1079.9	6.65	0.063	0.112	1.92E-05	3.04E-04	141.80	15115	0.284	0.929	0.088	0.261	3.04E-04	5.94E-04
SCR36-256	1.00E-03	0.0149	1003.3	0.1650	1081.2	6.67	0.063	0.112	3.55E-05	5.63E-04	173.39	12016	0.285	0.928	0.090	0.214	5.63E-04	7.87E-04
SCR36-258	7.60E-04	0.0152	1003.7	0.2430	1090.5	5.85	0.063	0.112	3.33E-05	5.29E-04	104.20	12279	0.220	0.920	0.063	0.216	5.29E-04	7.82E-04
SCR36-273	9.90E-04	0.0159	1004.2	0.3420	1087.5	4.98	0.063	0.112	5.47E-05	8.68E-04	62.89	6821	0.159	0.923	0.046	0.250	8.68E-04	5.17E-04
SCR36-274	8.50E-04	0.0191	1004.0	0.6470	1097.2	6.65	0.063	0.112	4.83E-05	7.67E-04	44.76	14274	0.284	0.915	0.030	0.265	7.67E-04	5.66E-04
SCR36-275	7.80E-04	0.0212	1003.9	0.1003	1074.4	5.00	0.063	0.112	3.11E-05	4.93E-04	212.58	8611	0.161	0.934	0.211	0.227	4.93E-04	6.53E-04

Parameters	
a	**1.13E-04**
b	**-2.6671**
c	**-0.2966**

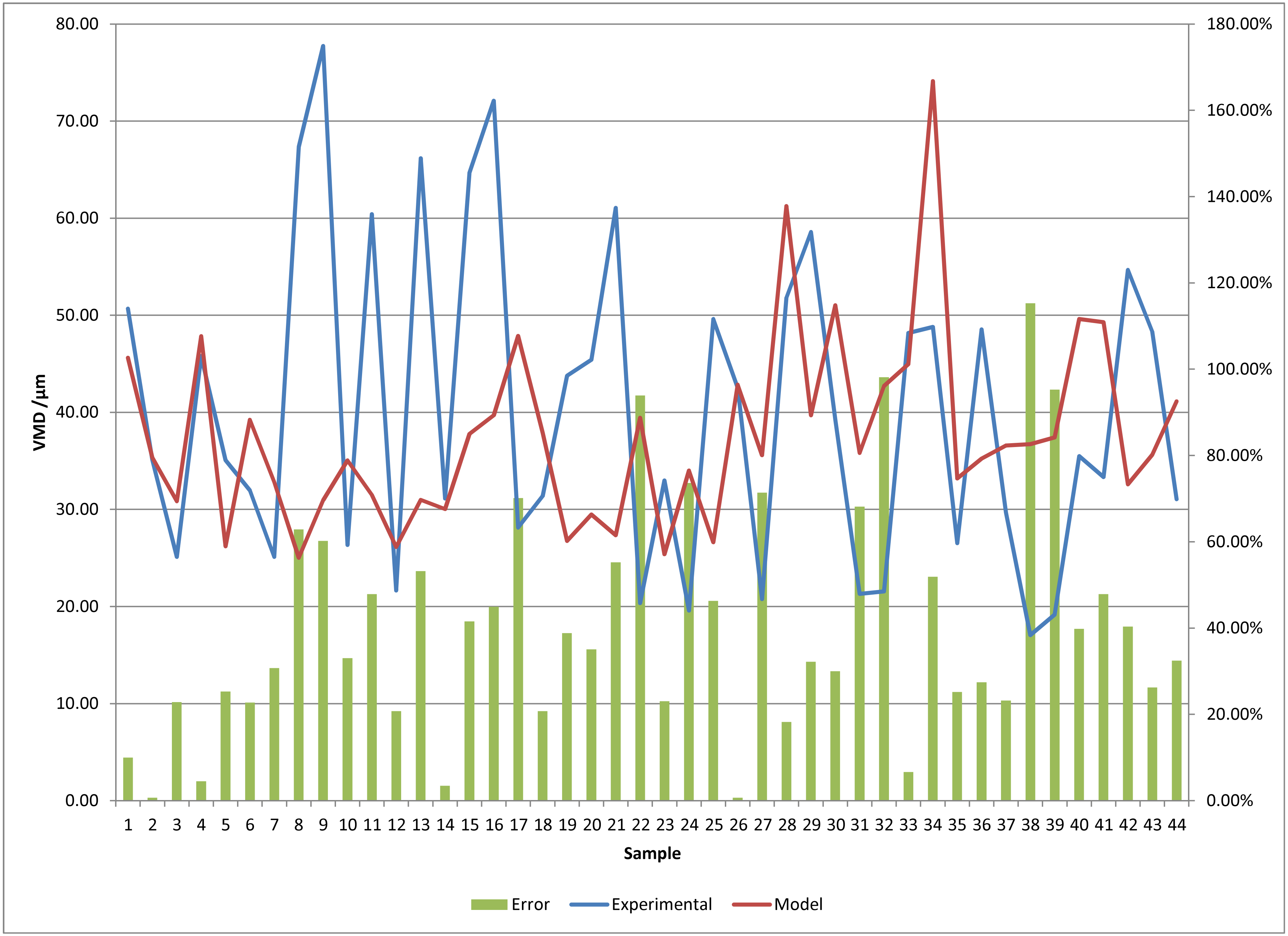
$$\alpha/_D = a(1 + b\phi)(We_T)^{-c}$$

Dimensionless Model Equation 6.8

Chatzi et. al (1989)

Batch No:	α /µm (experimental)	α /µm (model)	%Error	SS_{tot}	SS_{reg}	SS_{err}
SCR36-201	50.69	45.62	10.01%	111.758534	30.2446897	25.7259315
SCR36-202	35.11	35.36	0.70%	25.0841616	22.6675427	0.06118934
SCR36-203	25.12	30.86	22.84%	224.952275	85.7569058	32.9235725
SCR36-204	45.80	47.85	4.49%	32.2804753	59.8432776	4.21995448
SCR36-207	35.08	26.21	25.28%	25.3855662	193.360276	78.6236088
SCR36-208	31.96	39.22	22.73%	66.5596389	0.79864905	52.7764098
SCR36-209	25.10	32.81	30.73%	225.552612	53.3693094	59.4900445
SCR36-214	67.36	25.01	62.87%	742.104275	228.187341	1793.30754
SCR36-215	77.74	30.94	60.20%	1415.3841	84.2977486	2190.51814
SCR36-218	26.35	35.06	33.04%	189.569089	25.6368165	75.7792515
SCR36-219	60.40	31.50	47.85%	411.34293	74.3021767	835.294503
SCR36-221	21.64	26.13	20.74%	341.451603	195.721946	20.1452239
SCR36-222	66.18	30.98	53.20%	679.206521	83.6016736	1239.39104
SCR36-223	31.12	30.04	3.46%	80.9713662	101.533824	1.16206302
SCR36-224	64.64	37.78	41.56%	601.308421	5.49141061	721.726442
SCR36-225	72.09	39.70	44.94%	1022.18263	0.17891608	1049.40853
SCR36-226	28.14	47.88	70.15%	143.482284	60.2523675	389.693221
SCR36-227	31.38	37.89	20.74%	76.3597934	4.96967202	42.368812
SCR36-228	43.77	26.76	38.85%	13.3341162	178.361162	289.230676
SCR36-229	45.40	29.48	35.08%	27.8952025	113.280014	253.602418
SCR36-233	61.07	27.34	55.23%	438.969162	163.259086	1137.63726
SCR36-234	20.34	39.44	93.89%	391.185466	0.46438555	364.693526
SCR36-235	32.99	25.39	23.05%	50.8142162	217.039754	57.8186877
SCR36-237	19.58	34.00	73.65%	421.826248	37.4154096	207.982414
SCR36-238	49.61	26.63	46.32%	90.090298	181.952919	528.107215
SCR36-239	42.55	42.85	0.70%	5.91263435	7.43951392	0.08759015
SCR36-241	20.76	35.58	71.40%	374.748003	20.5800363	219.688323
SCR36-242	51.80	61.25	18.23%	136.459566	446.356817	89.2187431
SCR36-243	58.57	39.70	32.21%	340.461207	0.17176404	355.927283
SCR36-244	39.25	51.03	30.01%	0.75413435	119.011806	138.71333
SCR36-245	21.30	35.81	68.13%	354.132521	18.5522323	210.574312
SCR36-246	21.56	42.72	98.13%	344.414548	6.75219961	447.614781
SCR36-247	48.17	44.96	6.66%	64.8281162	23.4472086	10.299986
SCR36-249	48.79	74.12	51.91%	75.1964889	1155.99618	641.52546
SCR36-250	26.52	33.20	25.18%	184.91673	47.9129595	44.5755229
SCR36-251	48.55	35.23	27.44%	71.0917253	23.9281048	177.508381
SCR36-252	29.69	36.59	23.22%	108.751716	12.4815648	47.5476896
SCR36-253	17.06	36.73	115.29%	531.69023	11.4862624	386.880191
SCR36-254	19.16	37.42	95.29%	439.254912	7.29075883	333.364371
SCR36-256	35.48	49.61	39.82%	21.5148389	90.0640542	199.61783
SCR36-258	33.32	49.28	47.89%	46.2183662	83.8819964	254.629698
SCR36-273	54.67	32.60	40.37%	211.748798	56.5498104	487.153395
SCR36-274	48.30	35.63	26.22%	66.9384298	20.1116409	160.432403
SCR36-275	31.05	41.13	32.47%	82.2360434	1.02580102	101.631147
	Average Error		**40.73%**	11310.32	4355.02798	15758.6781

R^2	**-0.3933008**



VMD /µm
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
180.00%
160.00%
140.00%
120.00%
100.00%
80.00%
60.00%
40.00%
20.00%
0.00%
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44
Sample
Error
Experimental
Model

Batch No:	σ /kg.s^{-2}	μ_c /kg.m^{-1}.s^{-1}	ρ_c /kg.m^{-3}	μ_d /kg.m^{-1}.s^{-1}	ρ_d /kg.m^{-3}	N /s^{-1}	D /m	d /m	α /m	(α / D)	Re	We	Fr	(ρ_c / ρ_d)	(μ_c / μ_d)	
SCR36-201	7.20E-04	0.0177	1001.9	0.3290	1079.3	5.85	0.063	0.112	5.07E-05	8.05E-04	76.17	12828	0.220	0.928	0.054	0.229
SCR36-202	8.30E-04	0.0188	1002.7	0.4360	1075.0	4.95	0.063	0.112	3.51E-05	5.57E-04	48.44	7935	0.157	0.933	0.043	0.245
SCR36-203	9.10E-04	0.0149	1001.2	0.1560	1074.0	5.00	0.063	0.112	2.51E-05	3.99E-04	136.63	7378	0.161	0.932	0.096	0.259
SCR36-204	9.60E-04	0.0166	1001.4	0.2770	1076.3	6.65	0.063	0.112	4.58E-05	7.27E-04	102.55	12397	0.284	0.930	0.060	0.221
SCR36-207	1.61E-03	0.0150	1003.5	0.0869	1079.7	5.03	0.063	0.112	3.51E-05	5.57E-04	248.21	4248	0.163	0.929	0.173	0.259
SCR36-208	9.90E-04	0.0181	1002.2	0.2060	1085.8	6.70	0.063	0.112	3.20E-05	5.07E-04	140.16	12311	0.288	0.923	0.088	0.248
SCR36-209	5.40E-04	0.0182	1004.5	0.1580	1084.3	5.80	0.063	0.112	2.51E-05	3.98E-04	157.98	16890	0.216	0.926	0.115	0.278
SCR36-214	1.72E-03	0.0184	1003.9	0.2885	1089.4	5.07	0.063	0.112	6.74E-05	1.07E-03	75.94	4066	0.165	0.922	0.064	0.263
SCR36-215	1.25E-03	0.0153	1002.9	0.5005	1091.3	5.03	0.063	0.112	7.77E-05	1.23E-03	43.56	5531	0.163	0.919	0.031	0.248
SCR36-218	9.20E-04	0.0191	1004.6	0.1630	1087.2	5.03	0.063	0.112	2.64E-05	4.18E-04	133.25	7486	0.163	0.924	0.117	0.244
SCR36-219	8.00E-04	0.0154	1004.4	0.2833	1078.0	5.00	0.063	0.112	6.04E-05	9.59E-04	75.51	8423	0.161	0.932	0.054	0.261
SCR36-221	1.02E-03	0.0108	1004.4	0.1130	1070.0	4.98	0.063	0.112	2.16E-05	3.43E-04	187.29	6514	0.159	0.939	0.096	0.273
SCR36-222	2.15E-03	0.0145	1002.2	0.2864	1096.8	6.63	0.063	0.112	6.62E-05	1.05E-03	100.82	5613	0.283	0.914	0.051	0.249
SCR36-223	7.70E-04	0.0154	1002.1	0.1110	1073.1	5.03	0.063	0.112	3.11E-05	4.94E-04	193.13	8828	0.163	0.934	0.139	0.268
SCR36-224	1.04E-03	0.0154	1001.8	0.2902	1070.7	5.02	0.063	0.112	6.46E-05	1.03E-03	73.46	6479	0.162	0.936	0.053	0.227
SCR36-225	9.70E-04	0.0166	1003.4	0.4260	1093.2	4.97	0.063	0.112	7.21E-05	1.14E-03	50.59	6952	0.158	0.918	0.039	0.223
SCR36-226	8.70E-04	0.0151	1003.7	0.1280	1071.1	6.77	0.063	0.112	2.81E-05	4.47E-04	224.74	14096	0.294	0.937	0.118	0.226
SCR36-227	7.50E-04	0.0190	1003.5	0.1282	1072.6	5.07	0.063	0.112	3.14E-05	4.98E-04	168.25	9180	0.165	0.936	0.148	0.241
SCR36-228	8.10E-04	0.0184	1003.6	0.3083	1078.0	4.97	0.063	0.112	4.38E-05	6.95E-04	68.93	8209	0.158	0.931	0.060	0.277
SCR36-229	9.40E-04	0.0202	1003.4	0.2577	1088.1	5.02	0.063	0.112	4.54E-05	7.21E-04	84.07	7284	0.162	0.922	0.078	0.264
SCR36-233	2.28E-03	0.0151	1003.8	0.2124	1083.9	6.68	0.063	0.112	6.11E-05	9.69E-04	135.37	5310	0.287	0.926	0.071	0.262
SCR36-234	6.90E-04	0.0150	1003.5	0.1320	1081.7	6.65	0.063	0.112	2.03E-05	3.23E-04	216.29	17335	0.284	0.928	0.114	0.260
SCR36-235	1.02E-03	0.0191	1001.7	0.0916	1077.5	5.07	0.063	0.112	3.30E-05	5.24E-04	236.68	6781	0.165	0.930	0.209	0.277
SCR36-237	1.18E-03	0.0184	1003.1	0.0868	1078.4	6.70	0.063	0.112	1.96E-05	3.11E-04	330.46	10258	0.288	0.930	0.212	0.259
SCR36-238	2.11E-03	0.0154	1003.2	0.1656	1089.8	5.02	0.063	0.112	4.96E-05	7.87E-04	131.03	3250	0.162	0.921	0.093	0.247
SCR36-239	4.80E-04	0.0188	1004.2	0.1227	1067.5	5.08	0.063	0.112	4.26E-05	6.75E-04	175.53	14370	0.166	0.941	0.153	0.243
SCR36-241	9.60E-04	0.0148	1004.8	0.1890	1076.7	6.70	0.063	0.112	2.08E-05	3.30E-04	151.49	12589	0.288	0.933	0.078	0.261
SCR36-242	3.50E-04	0.0153	1003.2	0.1293	1068.3	6.70	0.063	0.112	5.18E-05	8.22E-04	219.71	34261	0.288	0.939	0.118	0.229
SCR36-243	6.90E-04	0.0154	1001.2	0.3208	1092.8	5.85	0.063	0.112	5.86E-05	9.30E-04	79.09	13553	0.220	0.916	0.048	0.250
SCR36-244	6.10E-04	0.0178	1001.6	0.4255	1084.1	6.67	0.063	0.112	3.93E-05	6.23E-04	67.42	19751	0.285	0.924	0.042	0.232
SCR36-245	7.80E-04	0.0188	1004.2	0.2470	1074.1	6.63	0.063	0.112	2.13E-05	3.38E-04	114.49	15151	0.283	0.935	0.076	0.266
SCR36-246	5.30E-04	0.0153	1001.7	0.1190	1075.4	6.65	0.063	0.112	2.16E-05	3.42E-04	238.52	22437	0.284	0.931	0.129	0.260
SCR36-247	7.40E-04	0.0165	1001.4	0.1979	1082.1	5.82	0.063	0.112	4.82E-05	7.65E-04	126.23	12371	0.217	0.925	0.083	0.230
SCR36-249	2.40E-04	0.0147	1001.2	0.2347	1084.1	6.63	0.063	0.112	4.88E-05	7.74E-04	121.61	49699	0.283	0.924	0.063	0.217
SCR36-250	1.12E-03	0.0171	1004.7	0.1890	1095.6	6.70	0.063	0.112	2.65E-05	4.21E-04	154.15	10980	0.288	0.917	0.090	0.264
SCR36-251	1.42E-03	0.0147	1003.7	0.5770	1091.5	6.67	0.063	0.112	4.86E-05	7.71E-04	50.05	8542	0.285	0.920	0.025	0.248
SCR36-252	5.60E-04	0.0171	1001.9	0.1665	1079.5	6.73	0.063	0.112	2.97E-05	4.71E-04	173.27	21853	0.291	0.928	0.103	0.275
SCR36-253	9.90E-04	0.0153	1001.0	0.2970	1079.5	5.88	0.063	0.112	1.71E-05	2.71E-04	84.87	9437	0.222	0.927	0.052	0.247
SCR36-254	7.90E-04	0.0177	1002.9	0.2010	1079.9	6.65	0.063	0.112	1.92E-05	3.04E-04	141.80	15115	0.284	0.929	0.088	0.261
SCR36-256	1.00E-03	0.0149	1003.3	0.1650	1081.2	6.67	0.063	0.112	3.55E-05	5.63E-04	173.39	12016	0.285	0.928	0.090	0.214
SCR36-258	7.60E-04	0.0152	1003.7	0.2430	1090.5	5.85	0.063	0.112	3.33E-05	5.29E-04	104.20	12279	0.220	0.920	0.063	0.216
SCR36-273	9.90E-04	0.0159	1004.2	0.3420	1087.5	4.98	0.063	0.112	5.47E-05	8.68E-04	62.89	6821	0.159	0.923	0.046	0.250
SCR36-274	8.50E-04	0.0191	1004.0	0.6470	1097.2	6.65	0.063	0.112	4.83E-05	7.67E-04	44.76	14274	0.284	0.915	0.030	0.265
SCR36-275	7.80E-04	0.0212	1003.9	0.1003	1074.4	5.00	0.063	0.112	3.11E-05	4.93E-04	212.58	8611	0.161	0.934	0.211	0.227

Batch No:	y	ym	α /µm (experimental)	α /µm (model)	%Error	SS_{tot}	SS_{reg}	SS_{err}
SCR36-201	1.97E-02	2.52E-02	50.69	39.63	21.82%	111.758534	0.23669209	122.281598
SCR36-202	2.85E-02	2.22E-02	35.11	45.09	28.42%	25.0841616	24.7069683	99.5808311
SCR36-203	3.98E-02	2.24E-02	25.12	44.74	78.11%	224.952275	21.3630752	384.961264
SCR36-204	2.18E-02	2.79E-02	45.80	35.90	21.62%	32.2804753	17.8203926	98.0696386
SCR36-207	2.85E-02	2.25E-02	35.08	44.51	26.89%	25.3855662	19.2987996	88.9522302
SCR36-208	3.13E-02	2.80E-02	31.96	35.69	11.67%	66.5596389	19.6113338	13.9124563
SCR36-209	3.98E-02	2.51E-02	25.10	39.90	58.95%	225.552612	0.04969869	218.906142
SCR36-214	1.48E-02	2.26E-02	67.36	44.29	34.26%	742.104275	17.3616466	532.449164
SCR36-215	1.29E-02	2.25E-02	77.74	44.51	42.74%	1415.3841	19.2987996	1104.1366
SCR36-218	3.80E-02	2.25E-02	26.35	44.51	68.92%	189.569089	19.2987996	329.83823
SCR36-219	1.66E-02	2.24E-02	60.40	44.74	25.93%	411.34293	21.3630752	245.22214
SCR36-221	4.62E-02	2.23E-02	21.64	44.86	107.28%	341.451603	22.4441759	538.979756
SCR36-222	1.51E-02	2.78E-02	66.18	35.97	45.65%	679.206521	17.2373634	912.848409
SCR36-223	3.21E-02	2.25E-02	31.12	44.51	43.03%	80.9713662	19.2987996	179.330906
SCR36-224	1.55E-02	2.24E-02	64.64	44.63	30.96%	601.308421	20.3147909	400.576114
SCR36-225	1.39E-02	2.22E-02	72.09	44.97	37.62%	1022.18263	23.5586262	735.378764
SCR36-226	3.55E-02	2.82E-02	28.14	35.42	25.86%	143.482284	22.0929177	52.9707207
SCR36-227	3.19E-02	2.26E-02	31.38	44.29	41.13%	76.3597934	17.3616466	166.542639
SCR36-228	2.28E-02	2.22E-02	43.77	44.97	2.75%	13.3341162	23.5586262	1.44512137
SCR36-229	2.20E-02	2.24E-02	45.40	44.63	1.71%	27.8952025	20.3147909	0.59969175
SCR36-233	1.64E-02	2.80E-02	61.07	35.76	41.45%	438.969162	19.0074868	640.664366
SCR36-234	4.92E-02	2.79E-02	20.34	35.90	76.48%	391.185466	17.8203926	242.019888
SCR36-235	3.03E-02	2.26E-02	32.99	44.29	34.24%	50.8142162	17.3616466	127.580188
SCR36-237	5.11E-02	2.80E-02	19.58	35.69	82.28%	421.826248	19.6113338	259.530184
SCR36-238	2.02E-02	2.24E-02	49.61	44.63	10.05%	90.090298	20.3147909	24.8442201
SCR36-239	2.35E-02	2.26E-02	42.55	44.17	3.81%	5.91263435	16.4394824	2.63403894
SCR36-241	4.82E-02	2.80E-02	20.76	35.69	71.92%	374.748003	19.6113338	222.903124
SCR36-242	1.93E-02	2.80E-02	51.80	35.69	31.10%	136.459566	19.6113338	259.534016
SCR36-243	1.71E-02	2.52E-02	58.57	39.63	32.33%	340.461207	0.23669209	358.65167
SCR36-244	2.55E-02	2.79E-02	39.25	35.83	8.72%	0.75413435	18.4104703	11.7123653
SCR36-245	4.69E-02	2.78E-02	21.30	35.97	68.86%	354.132521	17.2373634	215.109704
SCR36-246	4.64E-02	2.79E-02	21.56	35.90	66.50%	344.414548	17.8203926	205.549237
SCR36-247	2.08E-02	2.51E-02	48.17	39.81	17.36%	64.8281162	0.09686877	69.9368988
SCR36-249	2.05E-02	2.78E-02	48.79	35.97	26.28%	75.1964889	17.2373634	164.439108
SCR36-250	3.77E-02	2.80E-02	26.52	35.69	34.58%	184.91673	19.6113338	84.0878092
SCR36-251	2.06E-02	2.79E-02	48.55	35.83	26.20%	71.0917253	18.4104703	161.857765
SCR36-252	3.37E-02	2.81E-02	29.69	35.55	19.75%	108.751716	20.8390947	34.3797336
SCR36-253	5.86E-02	2.53E-02	17.06	39.46	131.29%	531.69023	0.43562864	501.687758
SCR36-254	5.22E-02	2.79E-02	19.16	35.90	87.35%	439.254912	17.8203926	280.126781
SCR36-256	2.82E-02	2.79E-02	35.48	35.83	0.98%	21.5148389	18.4104703	0.12087213
SCR36-258	3.00E-02	2.52E-02	33.32	39.63	18.94%	46.2183662	0.23669209	39.8400687
SCR36-273	1.83E-02	2.23E-02	54.67	44.86	17.95%	211.748798	22.4441759	96.3158217
SCR36-274	2.07E-02	2.79E-02	48.30	35.90	25.68%	66.9384298	17.8203926	153.834697
SCR36-275	3.22E-02	2.24E-02	31.05	44.74	44.09%	82.2360434	21.3630752	187.427867
			Average Error		**39.40%**	11310.32	744.799696	10571.7706

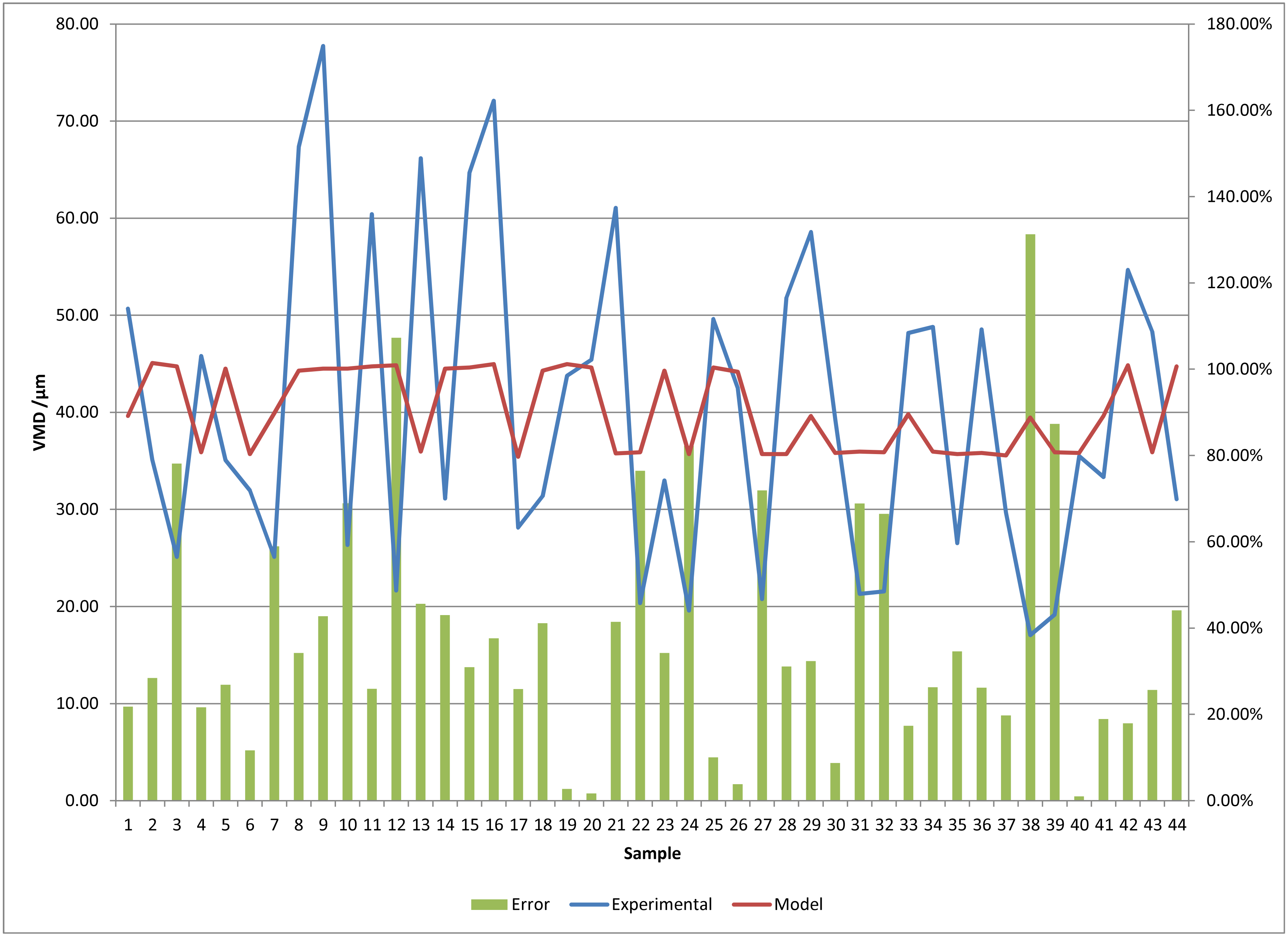
Parameters	
k'	**0.00645**
a	**0.77223**

$$\alpha_t^{-1} = k' N^a$$

Model Equation 6.9

Terblanche (2002) - simplified

R^2	**0.0652987**



80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
VMD /µm
180.00%
160.00%
140.00%
120.00%
100.00%
80.00%
60.00%
40.00%
20.00%
0.00%
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44
Sample
Error
Experimental
Model

Appendix F.2: MatLAB® Regression Programs

Appendix F.2.1: MatLAB® File – datam.mat

0.000804603	75.48159321	12827.53065	0.219777523	0.928286853	0.053313253	0.229
0.000557302	50.16636876	7935.282968	0.157355505	0.932744186	0.044655582	0.245
0.00039873	137.5066452	7377.760385	0.160550459	0.932216015	0.096129032	0.259
0.000726984	105.6048355	12397.29816	0.283997706	0.930409737	0.061710037	0.221
0.000556825	254.3572029	4248.251886	0.162698267	0.92942484	0.176886792	0.259
0.000507302	142.9401948	12310.78925	0.288284404	0.923006078	0.08960396	0.248
0.000398413	172.143468	16890.14327	0.216036697	0.926404132	0.125517241	0.278
0.001069206	77.96227132	4065.605534	0.164860347	0.921516431	0.065480427	0.263
0.001233968	46.18904129	5530.53539	0.162698267	0.918995693	0.032415254	0.248
0.000418254	134.06988	7486.083206	0.162698267	0.924025018	0.117901235	0.244
0.00095873	79.82429104	8423.458313	0.160550459	0.931725417	0.057462687	0.261
0.000343492	188.9586563	6513.960642	0.159481906	0.938691589	0.964285714	0.273
0.001050476	103.129362	5612.731584	0.282575943	0.913749088	0.051785714	0.249
0.000493968	193.1318976	8828.410187	0.162698267	0.933836548	0.138738739	0.268
0.001026032	79.25229853	6478.681084	0.161622579	0.935649575	0.057249071	0.227
0.001144286	237.8578768	6951.516605	0.158416922	0.917855836	0.183222958	0.223
0.000446667	228.304965	14095.54854	0.294049949	0.937074036	0.11984127	0.226
0.000498095	172.5564557	9180.003442	0.164860347	0.935577102	0.152	0.241
0.000694762	72.52658908	8208.908554	0.158416922	0.930983302	0.062798635	0.277
0.000720635	85.29654455	7284.388423	0.161622579	0.92215789	0.079527559	0.264
0.000969365	139.57133	5309.605593	0.286851937	0.926100194	0.073300971	0.262
0.000322857	217.9406683	17334.95338	0.283997706	0.927706388	0.114503817	0.26
0.000523651	242.6438298	6780.838828	0.164860347	0.929651972	0.213885778	0.277
0.000310794	336.9816254	10258.1519	0.288284404	0.930174332	0.216216216	0.259
0.00078746	133.9455017	3250.247905	0.161622579	0.920535878	0.095061728	0.247
0.000675397	205.120125	14369.62626	0.165946738	0.940702576	0.179047619	0.243
0.000329524	153.111922	12589.10146	0.288284404	0.933221882	0.079144385	0.261
0.000822222	539.0617474	34260.71623	0.288284404	0.939062061	0.290322581	0.229
0.000929683	81.58630457	13552.67351	0.219777523	0.916178624	0.049517685	0.25
0.000623016	916.4628115	19750.52479	0.285423038	0.923900009	0.568690096	0.232
0.000338095	115.422786	15150.79443	0.282575943	0.93492226	0.076734694	0.266
0.000342222	240.5419177	22436.70622	0.283997706	0.931467361	0.129661017	0.26
0.000764603	190.7003003	12371.02484	0.217280071	0.925422789	0.125954198	0.23
0.000774444	372.6091328	49698.51298	0.282575943	0.92353104	0.191906005	0.217
0.000420952	156.6372252	10980.07369	0.288284404	0.917031763	0.091935484	0.264
0.000770635	53.38463956	8542.294225	0.285423038	0.919560238	0.027171904	0.248
0.00047127	176.988992	21853.27332	0.291160041	0.928114868	0.104907975	0.275
0.000270794	86.62319768	9437.479265	0.222289246	0.927281149	0.05257732	0.247
0.000304127	144.6838508	15115.46071	0.283997706	0.928697102	0.089847716	0.261
0.000563175	176.596	12015.59184	0.285423038	0.927950425	0.091975309	0.214

0.000528889	131.1913877	12278.50406	0.219777523	0.920403485	0.078756477	0.216
0.000867778	65.18030114	6821.118514	0.159481906	0.923402299	0.048181818	0.25
0.000766667	48.58948359	14273.5438	0.283997706	0.915056507	0.03204698	0.265
0.000492857	223.4954717	8610.592846	0.160550459	0.934381981	0.222222222	0.227

Appendix F.2.2: MatLAB® File – Arai.mat

65932.94
52567.08
66895.99
79876.06
67046.68
73866.26
63738.53
55041.53
65692.74
52712.18
64930.91
92278.04
91288
65214.1
64978.7
59775.95
89556.53
53282.13
53939.06
49617.34
88462.43
88581.55
52908.1
72727.17
65069.51
54063.79
90570.8
87471.46
75727.13
74692.77
70548.81
86688.88
70289.96
89956.14
78380.96
90633.93
78551.39
76641.08

75024.22
89381.74
76915.12
62666.95
69601.32
47143.31

Appendix F.2.3: MatLAB® File – ter.mat

5.85
4.95
5
6.65
5.03
6.7
5.8
5.07
5.03
5.03
5
4.98
6.63
5.03
5.02
4.97
6.77
5.07
4.97
5.02
6.68
6.65
5.07
6.7
5.02
5.08
6.7
6.7
5.85
6.67
6.63
6.65
5.82
6.63
6.7
6.67

6.73
5.88
6.65
6.67
5.85
4.98
6.65
5

Appendix F.2.4: MatLAB® Files for Equation 6.5 Regression

Appendix F.2.4.1: MatLAB® File – Equ6_5fmin.m

```
clc;

clear all;

load datam.mat;

y = data(1:44,1)';

x = data(1:44,2:7);

z0 = [0.000001    0.1   0.1   -0.5  -20   -0.5   -1.5];

options=optimset('Display','iter','MaxFunEvals',10000,'MaxIter',10000,'TolFun',
1e-6,'TolX',1e-6);

zest = fminsearch(@Equ6_5,z0,options,x,y)
```

Appendix F.2.4.2: MatLAB® File – Equ6_5.m

```
function sse = Equ6_5(z0,x,y);

k = z0(1);

a = z0(2);

b = z0(3);

f = z0(4);

g = z0(5);

h = z0(6);

i = z0(7);

Re = x(1:44,1)';
```

```
We = x(1:44,2)';

Fr = x(1:44,3)';

dens = x(1:44,4)';

visc = x(1:44,5)';

holdup = x(1:44,6)';

yj = k*(Re.^a).*(We.^b).*(Fr.^f).*(dens.^g).*(visc.^h).*(holdup.^i);

j = yj-y;

sse = sum(j.^2);
```

Appendix F.2.5: MatLAB® Files for Hopff et. al. (1964) Equation Regression

Appendix F.2.5.1: MatLAB® File – Equ6_6fmin.m

```
clc;

clear all;

load datam.mat;

y = data(1:44,1)';

x = data(1:44,2:7);

z0 = [ 0.1 0.5 -1 -0.1];

options=optimset('Display','iter','MaxFunEvals',10000,'MaxIter',10000,'TolFun',
1e-6,'TolX',1e-6);

zest = fminsearch(@Equ6_6,z0,options,x,y)
```

Appendix F.2.5.2: MatLAB® File – Equ6_6.m

```
function sse = Equ6_6(z0,x,y);

K = z0(1);

a = z0(2);

b = z0(3);
```

```
c = z0(4);

Re = x(1:44,1)';

We = x(1:44,2)';

visc = x(1:44,5)';

yj = K*(Re.^a).*(We.^b).*(visc.^c);

j = yj-y;

sse = sum(j.^2);
```

Appendix F.2.6: MatLAB® Files for Arai et. al. (1977) Equation Regression

Appendix F.2.6.1: MatLAB® File – Equ6_7fmin.m

```
clc;

clear all;

load datam.mat;

load Arai.mat;

y = data(1:44,1)';

x = Arai;

z0 = [ 0.001 ];

options=optimset('Display','iter','MaxFunEvals',10000,'MaxIter',10000,'TolFun',
1e-6,'TolX',1e-6);

zest = fminsearch(@Equ6_7,z0,options,x,y)
```

Appendix F.2.6.2: MatLAB® File – Equ6_7.m

```
function sse = Equ6_7(z0,x,y);

K = z0(1);

x = x';

yj = K*(x.^(-0.75));
```

```
j = yj-y;

sse = sum(j.^2);
```

Appendix F.2.7: MatLAB® Files for Chatzi et. al (1989) Equation Regression

Appendix F.2.7.1: MatLAB® File – Equ2_9fmin.m

```
clc;

clear all;

load datam.mat;

y = data(1:44,1)';

x = data(1:44,2:7);

z0 = [ 0.00001    -2   0.1 ];

options=optimset('Display','iter','MaxFunEvals',10000,'MaxIter',10000,'TolFun',
1e-6,'TolX',1e-6);

zest = fminsearch(@Equ2_9,z0,options,x,y)
```

Appendix F.2.7.2: MatLAB® File – Equ2_9.m

```
function sse = Equ2_9(z0,x,y);

a = z0(1);

b = z0(2);

c = z0(3);

We = x(1:44,2)';

holdup = x(1:44,6)';

yj = a*(1+b*holdup).*(We.^c);

j = yj-y;

sse = sum(j.^2);
```

Appendix F.2.8: MatLAB® Files for Terblanche (2002), Simplified Equation Regression

Appendix F.2.8.1: MatLAB® File – Equ6_9fmin.m

```
clc;

clear all;

load datam.mat;

load ter.mat;

y = data(1:44,1)';

y = 1./(y*0.063*1000000);

x = ter;

z0 = [ 0.001 0.1 ];

options=optimset('Display','iter','MaxFunEvals',10000,'MaxIter',10000,'TolFun',
1e-6,'TolX',1e-6);

zest = fminsearch(@Equ6_9,z0,options,x,y)
```

Appendix F.2.8.2: MatLAB® File – Equ6_9.m

```
function sse = Equ6_9(z0,x,y);

k = z0(1);

a = z0(2);

N = x';

yj = k*(N.^a);

j = yj-y;

sse = sum(j.^2);
```

Appendix F.3: Development of Equation 6.3

The average particle size quantified by the VMD (α) is a function of the system parameters identified in Table 6.1.

$$\alpha = f(d, D, h, N_b, N_i, a, N, P, H, t, \phi, \rho_d, \rho_c, \mu_d, \mu_c, \sigma, g) \tag{6.0}$$

The identified dimensions for the equation are length (meters), time (seconds) & mass (kilograms) represented by the identified parameters D (m), N (s^{-1}) ρ_d ($kg.m^{-3}$).One possible form Equation 6.0 can take on is:

$$\pi_1 = k \prod_{i=2}^{n} \pi_i^{j_i} \tag{F.3.1}$$

Fitting equation 6.0 to the form of F.3.1:

$$\alpha = k d^b D^c h^e N_b{}^f N_i{}^l a^m N^n P^p H^q t^r \phi^s \rho_d{}^u \rho_c{}^v \mu_d{}^w \mu_c{}^x \sigma^y g^z \tag{F.3.2}$$

To obtain dimensionally homogenous model terms, each π term is divided through by the identified parameters D (m), N (s^{-1}) ρ_d ($kg.m^{-3}$) and the dimensions' exponents are equated to zero to obtain dimensionally homogenous terms e.g. μ_d:

$$\left(\frac{\mu_d\{kg^1.m^{-1}.s^{-1}\}}{D\{m^1\}^c N\{s^{-1}\}^n \rho_d\{kg^1.m^{-3}\}^u}\right)^w \tag{F.3.3a}$$

$$\begin{array}{c} kg \\ m \\ s \end{array} \begin{bmatrix} 0 = 1 - u \\ 0 = -1 - c + 3u \\ 0 = -1 + n \end{bmatrix} \tag{F.3.3b}$$

$$\left(\frac{\mu_d}{D^2 N \rho_d}\right)^w \tag{F.3.3c}$$

After each π term is dimensionally homogenous equation F.3.2 evolves to equation 6.1:

$$\left(\frac{\alpha}{D}\right) = k\left(\frac{d}{D}\right)^b \left(\frac{D}{D}\right)^c \left(\frac{h}{D}\right)^e (N_b)^f (N_i)^l \left(\frac{a}{D}\right)^m \left(\frac{N}{N}\right)^n \left(\frac{P}{N^3 D^5 \rho_d}\right)^p \left(\frac{H}{D}\right)^q (tN)^r (\varphi)^s \left(\frac{\rho_d}{\rho_d}\right)^u \left(\frac{\rho_c}{\rho_d}\right)^q$$

$$\times \left(\frac{\mu_d}{ND^2\rho_d}\right)^w \left(\frac{\mu_c}{ND^2\rho_d}\right)^x \left(\frac{\sigma}{N^2D^3\rho_d}\right)^y \left(\frac{g}{N^2 D}\right)^z \tag{6.1}$$

The PSD of the MVP system has reached dynamic equilibrium after the emulsification period and before catalysis the PSD will be independent of the emulsification time and (tN) will become constant. For geometric similarity: (N_b);$\left(\frac{d}{D}\right)$;$\left(\frac{h}{D}\right)$;$\left(\frac{H}{D}\right)$ becomes constant and for the same scale reactor $\left(\frac{a}{D}\right)$ becomes constant and results in equation 6.2:

$$\left(\frac{\alpha}{D}\right) = k(N_i)^l \left(\frac{P}{N^3D^5\rho_d}\right)^p (tN)^r (\varphi)^s \left(\frac{\rho_c}{\rho_d}\right)^q \left(\frac{\mu_d}{ND^2\rho_d}\right)^w \left(\frac{\mu_c}{ND^2\rho_d}\right)^x \left(\frac{\sigma}{N^2D^3\rho_d}\right)^y \left(\frac{g}{N^2D}\right)^z \tag{6.2}$$

Rearranging equation 6.2 and substituting in engineering dimensionless numbers results in:

$$\left(\frac{\alpha}{D}\right) = k\left(\frac{ND^2\rho_d}{\mu_d}\right)^a \left(\frac{N^2D^3\rho_d}{\mu_d}\right)^b \left(\frac{P}{N^3D^5\rho_d}\right)^e \left(\frac{N^2D}{g}\right)^f \left(\frac{\rho_c}{\rho_d}\right)^g \left(\frac{\mu_c}{\mu_d}\right)^h \phi^i \tag{6.3a}$$

$$\left(\frac{\alpha}{D}\right) = kRe_d^a We_d^b Ne_d^e Fr^f \left(\frac{\rho_c}{\rho_d}\right)^g \left(\frac{\mu_c}{\mu_d}\right)^h \phi^i \tag{6.3b}$$

The engineering dimensionless numbers used are:

Modified Newton (Power) Number: $Ne = \left(\frac{P}{N^3D^5\rho_d}\right)$

Modified Reynolds Number: $\mathrm{Re} = \left(\frac{ND^2\rho}{\mu}\right)$

Modified Weber Number: $We = \left(\frac{N^2D^3\rho}{\sigma}\right)$

Modified Froude Number: $Fr = \left(\frac{N^2D}{g}\right)$